THE GEOCHEMISTRY OF MERCURY AT NGAWHA SPRINGS, NEW ZEALAND.

by

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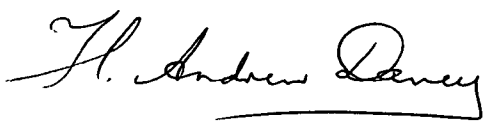
To the best of my knowledge this thesis contains no material by another author, except where due reference is made.



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ABSTRACT

Currently cinnabar is depositing at Ngawha Springs from mercury transported as the element. Much of the deposition is weather dependent and all ore occurs in the uppermost few metres of the ground. Field conditions and laboratory experiments demonstrate that deposition requires oxygen and that the presence of chloride enhances the oxidation of mercury. The deposition of the cinnabar proceeds according to the reaction:

$$Hg^{2+} + 2e^- \rightleftarrows Hg \qquad E^o = +0.851 \text{ v and}$$

$$4H^+ + O_2 + 4e^- \rightleftarrows 2H_2O \qquad E^o = +1.229 \text{ v.}$$

That is $$2Hg + 4H^+ + O_2 \rightleftarrows 2Hg^{2+} + 2H_2O \qquad E^o = +0.378 \text{ v.}$$

The mercury II thus formed rapidly reacts with reduced-sulphur species from geothermal and biogenic sources to produce cinnabar.

Biogenic replacement of organic material by metal sulphides is an important deposition mechanism, for it is responsible for the bulk of the richest cinnabar occurrences via the marcasite pseudomorphing of vegetation debris adjacent to the geothermal emanations. The oxidative destruction of the pseudomorphs yields the high concentrations of cinnabar by removing all but the resistant mercury sulphide.

Investigation of the mercury species and their concentrations in gases, waters, soils, biota and rocks showed that mercury II compounds generally dominate in the solid materials, where as elemental mercury dominates in the subterranean fluids and mercury adsorbed onto particulate matter dominates most surface-waters. Organo-mercurials and cold, dilute-acid-extractable mercury did not dominate anywhere. The source of the anomalous mercury is two sedimentary facies which underlie the

Ngawha Basin: the basement and the subordinate olistostrome known as the Northland Chaos Breccia.

Radiocarbon fourteen dating, mass-balance analyses and flux calculations reveal that the ore deposits are nearly 6900 years old, and that ca. 520 kg of mercury enter the Ngawha Basin and environs each year. About 44% of the mercury diffuses into the air and ca. 5% is carried off by fumarole gases; of the remaining mercury only about 4.5% occurs in ore-grade concentrations.

The deposition and attrition mechanisms for the Ngawha deposits (which are closely compatable with many other mercury deposits) yield explanations for the traits of mercury deposits. Nearly all the traits are inherent in the mechanisms developed for Ngawha. Similarly means for more efficient mercury exploration result, as well as applications for pollution abatement and geothermal anomaly detection.

THE GEOCHEMISTRY OF MERCURY AT NGAWHA SPRINGS, NEW ZEALAND

THE OBJECTIVES

The thesis is an investigation into the movement of mercury in an area of natural emissions associated with cinnabar occurrences. In particular, the ore-deposition reactions were studied in order to find the chemical species and mechanisms involved in the mobilsation, transport, deposition and dispersion processes. The mercury fluxes involved in the processes were also estimated.

Another reason for the study is that many of the published 'feasible mechanisms' for mercury deposition are incompatable with natural conditions.

The data and understanding obtained from the study of real systems should also explain at least some of the many peculiarities common to mercury deposits, yield ideas useful for the control and abatement of mercury pollution and indicate more efficient ways to explore for mercury deposits (and perhaps other ore-deposits).

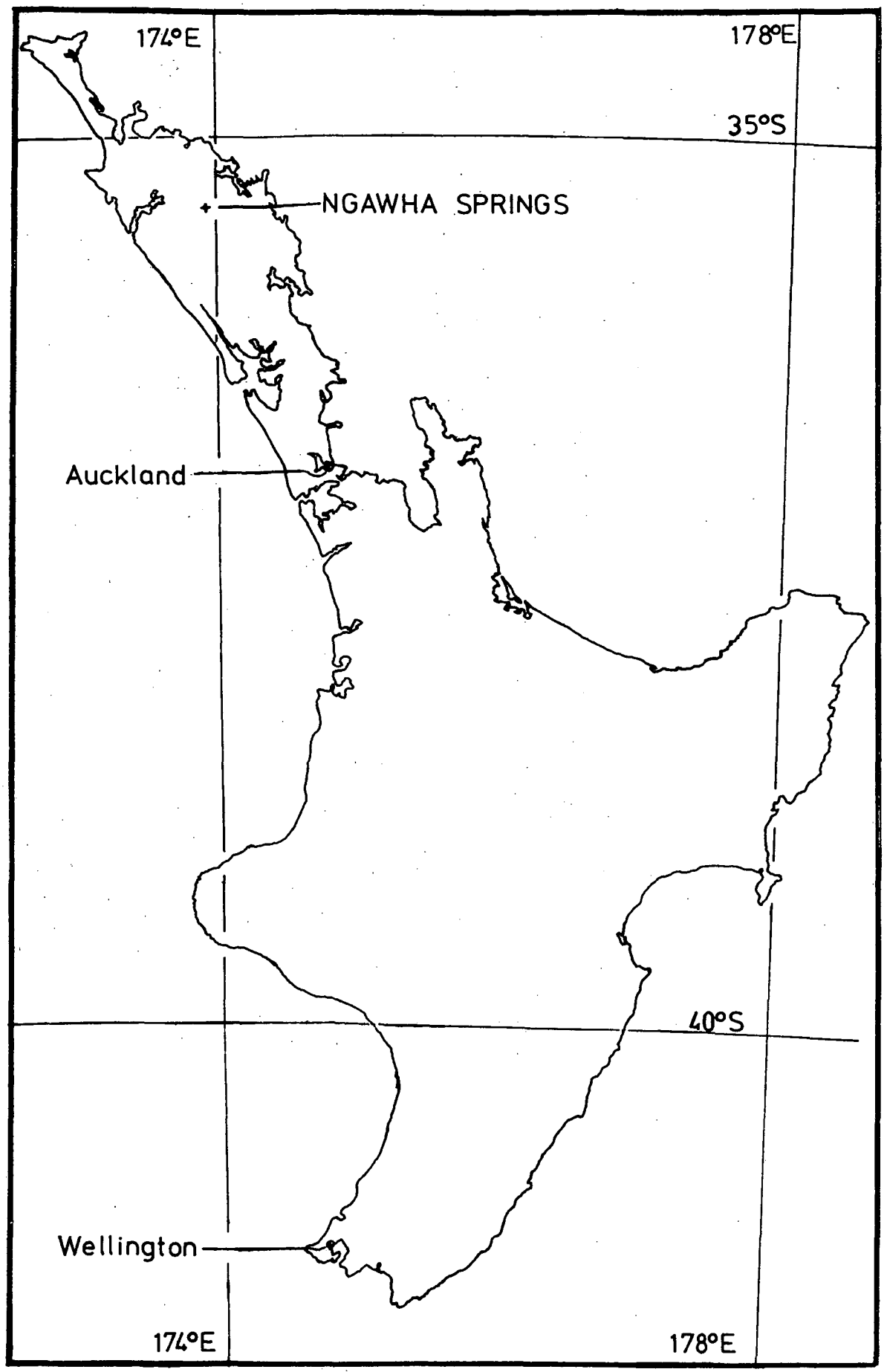

Figure (1.1) North Island of New Zealand.

CHAPTER ONE NGAWHA SPRINGS

(1.1) THE FIELD AREA

a. Geography

The area chosen for the thesis is the Ngawha Basin, a region containing hot springs associated with recent cinnabar deposition in far northern New Zealand (Figure (1.1)). Adjacent to the sites of most intense geothermal exhalations is the small town of Ngawha Springs, which is 250 km north-north-west from Auckland (by road), and situated in the Bay of Islands county (Figure (1.2)). At the northern end of the basin, alongside State Highway 12, is the smaller town of Ngawha which houses less than 25 persons.

The shallow Ngawha Basin (Figure (1.3)) occupies about 15 km^2 and is 160 - 225 m above sea level (Gough, 1965). The surrounding hills are less than 390 m high, and most hills reach no more than 280 m. The climate is warm - temperate and maritine: the sea is 40 km to the east and 65 km to the west. Rainfall averages 1300 to 1550 mm per annum and is fairly evenly distributed throughout the year ('Grasslands', 1975).

The basin is drained by two equitable streams: the Mangatawai and the Mangamutu (Figure (1.3)). The upper portion of the latter is also called the Ngawha Stream. Both streams flow north-east before they confluence 2 km from the basin, 17 km away they join the Waitangi River which meets the sea near Paihia 25 km from Ngawha Springs.

b. Industry

Approximately 30% of the basin area is under pasture for beef, dairy and recreation, the remaining cover is tea-tree scrub, dense gorse or swamp. Much of the valley was once well forested, however kauri-gum diggers have entirely removed the trees, probably late last century. Currently a locally important industry is hostelry for the approximately 1500 persons who visit the three balneal establishments at Ngawha Springs each year.

The town has a permanent population of about 60 persons (ca. 1976), however the famed pools attract scores of sufferers of rheumatics, athritis and dermatitus. (The pools have probably been used as such since early Maori times.) Apart from a small general store, the town depends almost entirely on Kaikohe for goods and services.

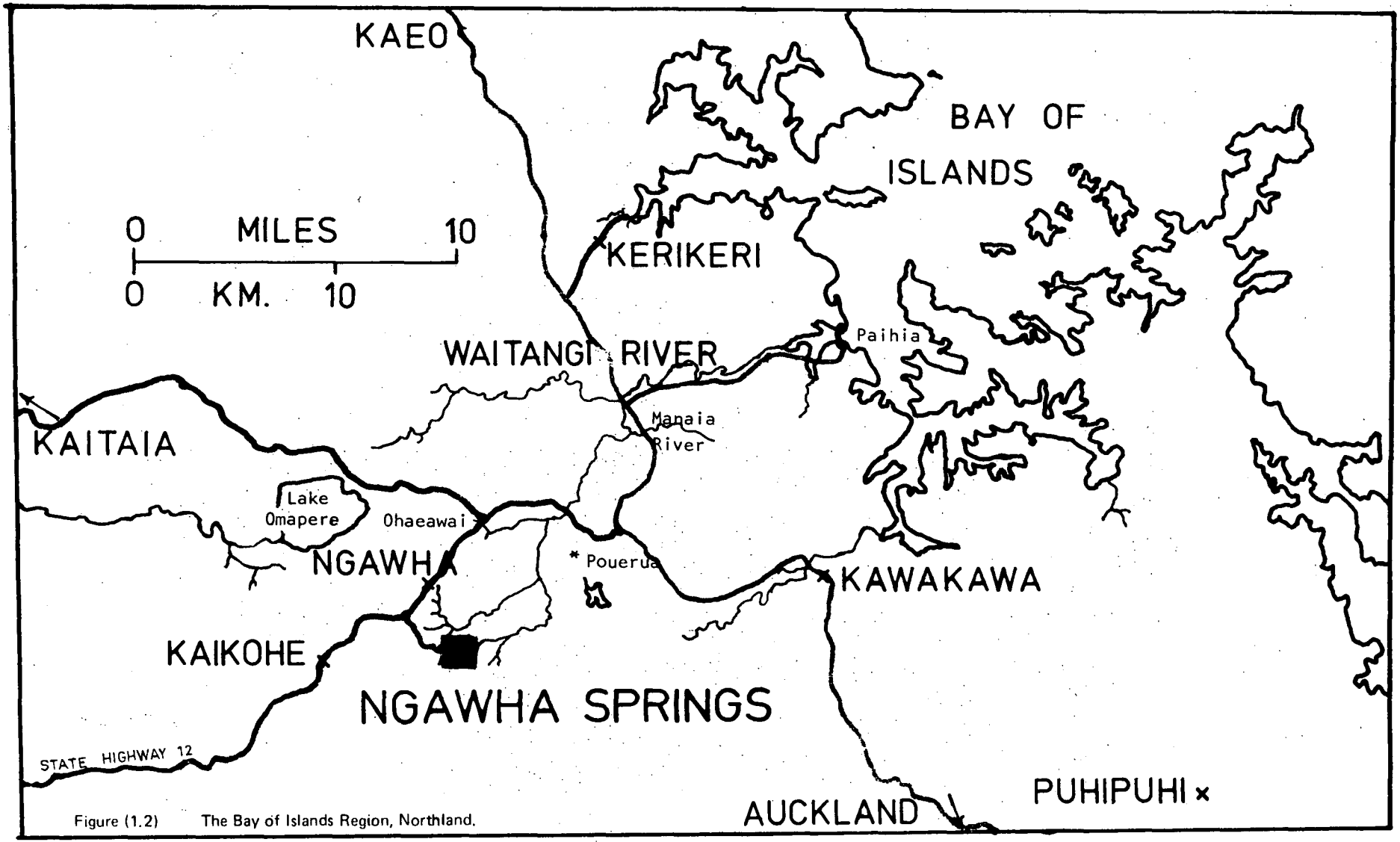

Figure (1.2) The Bay of Islands Region, Northland.

c. Mining

Between 1895 and 1934 the intermittent mining of cinnabar was the mainstay of Ngawha Springs, and the only significant local industry. About 85 tonnes of mercury were smelted during the sixty years of prospecting and mining to 1934 and now the area is virtually exhausted of ore-grade concentrations of mercury.

The presence of mercury was known to Europeans as early at 1866 (Bell and Clarke, 1909). In 1870 Captain Hutton found cinnabar and mercury on the shores of Tuwhakino Pond which led to more extensive prospecting by G.F. Dickeson in 1873. Subsequently F. Earl leased the property from the Maoris and retorted some mercury. On expiry of the lease, the property passed through many hands and several companies were formed to exploit the mercury deposits. Production of mercury varied considerably, although most frequently it had ceased. Two companies have taken by far most of the mercury mined: The Ohaeawai Quicksilver Mines (1895 - 97) and The Kaikohe Development Company (1928 - 34). The former smelted ore averaging 1.5% mercury, and by ca. 1931 the latter was using ore averaging 0.002% mercury (Henderson, 1944) in spite of the many thousands of bores sunk.

The various mining companies and prospectors had considerable difficulty collecting the mercury due to the presence of natural oils (which prevented the cohesion of liquid mercury) and the lack of water to cool retort condensers. Consequently the efficiency of mercury extraction was usually near 70% of that present in the ore, and led to lower profits than anticipated.

d. Geothermal Power

During the early to mid nineteen sixties the suitability of the area for geothermal energy was investigated and more recently detailed work was commenced. By late 1978 three deep bore-holes had been sunk and more are anticipated (Lyon, 1978). (No new deep drill-hole data was available at the time of writing the thesis).

The likelihood of the development of the area to produce electrical power is still uncertain, however it has been anticipated that the area could produce up to 50% of the output from Wairaki (Banwell, 1965). The energy short-fall during some winters and the high cost of oil (which is used at Marsden Point, some 100 km south-east) makes electricity generation seem probable.

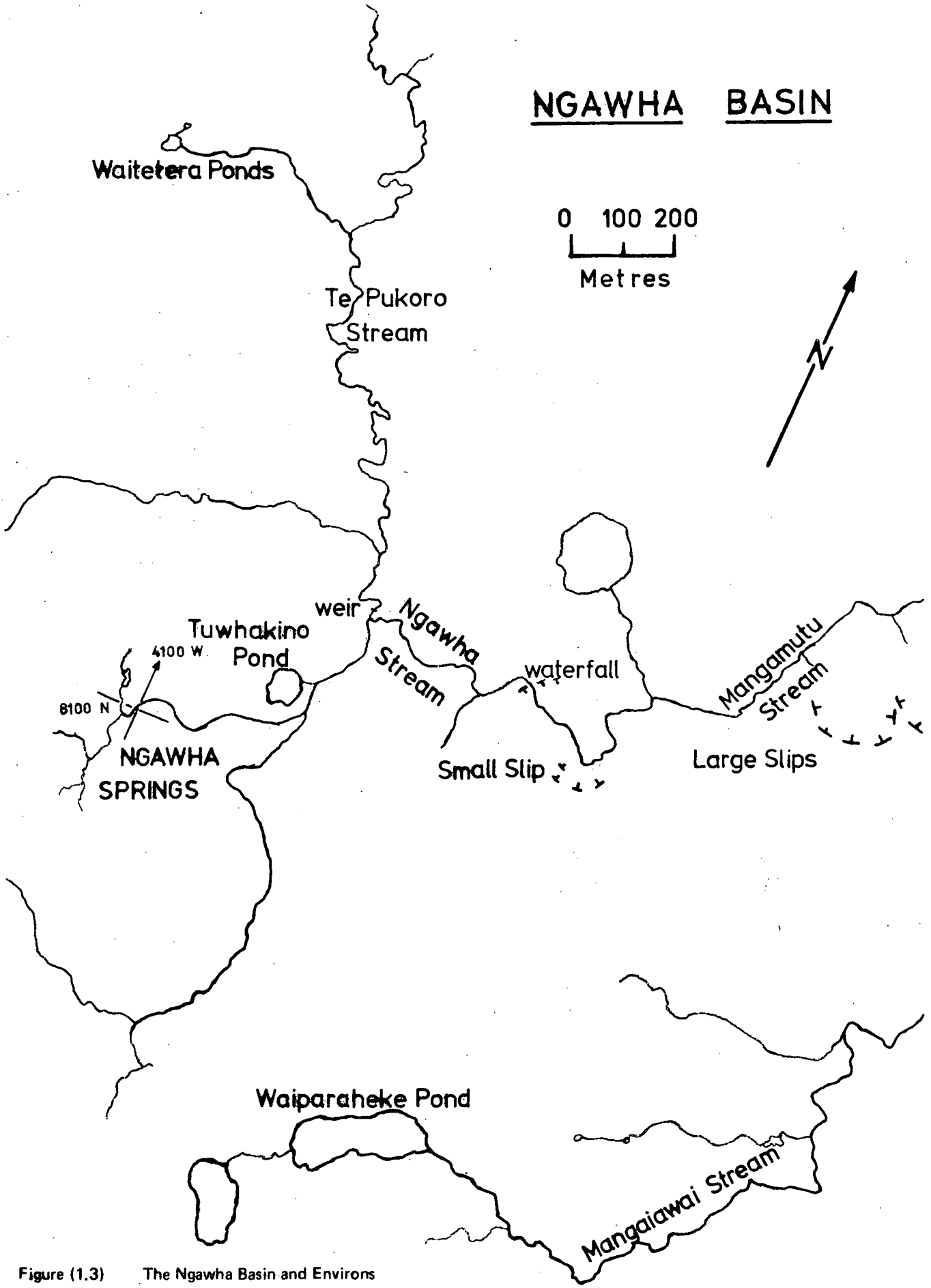

Figure (1.3) The Ngawha Basin and Environs

(1.2) PUBLISHED WORK.

All early work related to the exploitation of the springs area for mercury. About 35 years ago interest began to change to the development of the springs for balneal purposes, and in the last 15 years interest in the harnessing of the geothermal energy has greatly increased.

The first detailed description of the deposits is the work of Griffiths, (1898), who describes the area prior to the large-scale prospecting and mining which he supervised between 1895 and 1897. In 1906 Park also described the springs and their relation to cinnabar deposition. Bell and Clarke (1909) gave the first good account of the geology of the area and mapped the entire basin. They found all the now known occurrences of geothermal emanations and analysed minerals, waters and gases. Their interpretation of the geological history of the basin has remained unchanged to this day but for additional detail.

During 1935 a detailed magnetic survey and some boring was carried out in the central hot spring zone and environs (Jones, 1939). Basalt was found to border the entire south-eastern side of the main (central) thermal zone (Figure (3.7)). Henderson (1944) redescribed the cinnabar deposits which had been further exploited between 1928 and 1934, and quoted the quantity of mercury taken (18 tons, 15 cwt, and 65 lb).

A 21 page paper detailing most hydrothermal emanations, with a brief description of each site plus a few water and gas analyses, was published by Fleming in 1945. The presence of terraces about many large pools was also noted and explained in terms of a step-wise drainage of the once flooded basin. The aim of the investigation was to find balneal waters suitable for development. Based partly on the work done by Jones (1939), Healy (1945) and Griffiths (1898) it was suggested that boring in the basalt near Tuwhakino Pond would supply the most suitable water. Fleming's detailed map of the Tuwhakino area is still applicable today but for some changes, due to erosion and silting.

During the early to mid-nineteen sixties, there were a number of regional and local investigations to assess the potential and suitability of the area for harnessing geothermal energy. The studies are summarised by Thompson and Kermode (1965) and more detailed data is available in circulars of the D.S.I.R.* and several other publications. The main articles of interest are Skinner (1966) for geology and Ellis and Mahon (1966) for geochemistry. The investigations cover the fields of geology, geochemistry, geophysics and isotope geology.

* Department of Scientific and Industrial Research (New Zealand).

A study on the hydrogen and oxygen isotopes was published by McDonald (1966) in which he concluded that the springs are of meteoric origin and that the thermal pools undergo considerable non-equilibrium evaporation. Also in 1966, Wilson published a paper which included a few sulphur isotope data for the Ngawha waters. Carbon thirteen ratios were also measured in the gases (Stewart, 1975) but gave erratic temperatures.

Based on analyses of the 591 m (1940 feet) bore (NG1) sank in 1964, Ellis (1970) gives the geochemical data for the Ngawha waters. His data indicate that the Ngawha fluids are unusually gas-rich and very high in boron compared to most hot springs.

The upper Tuwhakino area was again prospected for mercury (and sulphur) in 1971 (Rabone). The samples were taken by shallow augering and averaged just over 0.15% Hg. It was estimated that there were about 300 tonnes of mercury present at concentrations above 0.1%.

In late 1973 the basin was mapped and sampled for rocks, cinnabar and geothermal fluids. During that time cinnabar deposition was observed (Davey and van Moort, 1974), and subsequently the physical and chemical conditions and the mechanism for deposition were discovered (Davey, 1974).

Samples collected by Davey in 1973 and 1975 were radiocarbon dated by The Institute of Nuclear Sciences (Wellington, New Zealand) in 1976 and show that the geothermal activity is about 6900 years old. Sufficient data had then been collected to estimate the total flux of mercury in the geothermal system and the major components (Davey, 1976).

Also in 1976 a sulphate reducing bacteria which is responsible for the deposition of significant amounts of cinnabar and iron sulphides in stream sediments was isolated (Davey, 1977).

Following the urgent need for energy based on New Zealand resources, more intense studies of the Ngawha geothermal system were commenced in 1977 (Lyon, 1977) and included isotopic and geochemical analyses. Subsequently Giggenbach and Lyon (1977) have made tentative interpretations of the chemical equilibria, thermal regimes and hydrology of the sub-basin area. Concommitant with the study, the Ministry of Works had sunk at least three more deep drill-holes by late 1978 (Lyon, 1978); work is continuing. One bore is ca. 1400 m deep.

CHAPTER TWO MERCURY

(2.1) PROPERTIES

Mercury, a heavy metal, is the eightieth element, consists of seven stable isotopes (between 196 and 204 a.m.u.) and it has an average atomic mass of 200.59 (Nier, 1950). Between -38.9 and 356.6°C it is a liquid (quicksilver) of density 13.59 g/cm^3 (Weast, 1976). The element is relatively inert, however it can form a large variety of compounds, including some very toxic organomercurials (Lu, Berteau and Clegg, 1972). Mercury is also one of the most chalcophile elements. The liquid element has a significant vapour pressure under normal biospheric conditions (e.g. Davey ,1974 : ca. 12 μg/l at 10°C to 65 μg/l at 35°C). The element also has a stable significant solubility in water: 0.05 ppm, 10°; 0.07 ppm, 35° and 0.5 ppm at 100°C in distilled water. (Glew and Hames, 1971), and is more soluble in natural waters (Aidin' yan, 1962; Davey and van Moort, 1974).

(2.2) MERCURY IN NATURE

The element and compounds are widely distributed in nature in spite of the low crustal abundance of mercury, ca. 0.07 ppm from data in Wedepohl, 1970; Fleischer, 1970; Ehmann and Lovering, 1967; Table (A.9). Economic concentrations of mercury are rare, and chiefly occur as cinnabar deposits (White, 1967). Background levels are commonly below 0.03 ppm, however some regions contain appreciably higher concentrations (Fleischer, 1970). There does not seem to be any recognisable background control for mercury concentrations in geological material except by regional bases. Within a given region background concentrations may vary considerably, even with physical conditions such as weather (McCarthy, Meuschke, Ficklin and Learned, 1970). Generally mercury concentrations do not exceed 5 ppm unless mineralisation is nearby.

A considerable number of studies have been made on mercury in natural environments since the development of analytical techniques able to detect subnanogram quantities of mercury (Hatch and Ott, 1964; Stainton , 1971; Weissberg, 1969), and the subsequent realisation of the insidious toxicity of mercury at concentrations near one part per million (Westöö, 1968; Jenson and Jernelov, 1969; Wood, 1971 and 1972; Krenkel, 1973 and 1974; Parks, 1973; Kokot, 1974; Bloom, 1975; Hoggins and Brooks, 1973).

Much work has also been done on mercury anomalies for geochemical prospecting for ore-bodies (Barringer, 1971; Koksoy and Bradshaw, 1965; Ozerova, 1962;

Table (2.1)

Some Properties of Mercury.

Property		Reference
Melting point	$-38.87^{o}C$	a
Boiling point	$356.58^{o}C$	a
Vapour pressure ($0^{o}C$)	2 µg/l	a
" " ($25^{o}C$)	22 µg/l	a
" " ($100^{o}C$)	3200 µg/l	a
Aqueous solubility ($25^{o}C$)	0.055 ppm	b
" " ($100^{o}C$)	0.5 ppm	b
Oxidation potential (Hg/Hg^{2+})	.851 V	c
Heat of vaporization	61.5 kJ/Mole	a
Toxic limit in air	10^{-4} µg/l	d

a - Weast, 1976

b - Glew and Hames, 1971

c - Krauskopf, 1967; Weast, 1976

d - Royal Australian Chemical Institute leaflet on chemical toxocity.

1973 and 1978; McNerney and Buseck, 1973; Hoggins, 1972; Friedrich and Hawkes, 1966; McCarthy, Vaughn, Learned and Meuschke, 1969). Many deposits have wide dispersion haloes of mercury as well as anomalously high concentrations in stream sediments and biota (Hoggins and Brooks, 1973). Saukov (1946) was probably the first person to recognise the importance of mercury to prospecting, and nowadays geochemical prospecting is a well established practice.

The other major area of work relevant to the thesis concerns the transport of mercury in 'ore-solutions', which until recently was carried out only in laboratory solutions or by theoretical considerations (usually from insufficient accurate data) (e.g. Krauskopf, 1951; Dickson, 1964; Scharwzenbach and Widmer, 1963; Barnes, Romberger and Stemprok, 1967; Khodakovsky, Popova and Ozerova, 1975). Transport is discussed in detail later in this chapter.

a. Rocks

Mercury concentrations in rocks follow provinciality rather than rock-type (Fleischer, 1970). Very few rocks are able to be associated with 'typical mercury concentrations', however most rocks (not near mineralization) contain from 0.01 to 0.5 ppm total mercury (Golonya and Volobeyev, 1970; Marovski and Wedepohl, 1972). High grade metamorphic rocks are no exception in spite of anticipated low mercury concentration (Jovanic and Reed, 1968; Ozerova and Aidin'yan 1966a and 1966b). Notably metamorphic rocks are rarely associated with mercury deposition (Moiseyev, 1971). The main rock-type distinguishable from others is organic-rich shales which commonly have mercury concentrations between 0.1 - 2 ppm. Mercury reaches very high concentrations around many ores deposits, especially sulphide ore bodies. The upper limit of mercury in mineralised areas in unaltered rock may be as high as 8,000 ppm (Jonasson, 1970), and anomalies may persist for over one kilometre (Ozerova, 1962). Even in non-mercury minerals the mercury contents may be very high (Weissberg and Wodzicki, 1970), and rarely over 1% (Ozerova, 1973).

The form(s) of mercury in rocks (and soils) is not well understood, and there is much data held by mining companies. Mercury is known to be present as the element, ions, inorganic and organic compounds which may be adsorbed, part of crystal structures or separate phases in the various components of a rock (Krauskopf, 1956; Fedorchuk, 1963; Ozerova and Fedorchuk, 1963; Dvornikov, 1967; Dall'aglio, 1968; Bradshaw and Koksoy, 1968; Dvornikov and Zakrenichnaya, 1970; James and Oleckie, 1974; Klusman and Landress, 1978). It is suggested that organomercurials are not significant in non-organic rocks (Andren and Harriss, 1973). From the above it seems that most mercury in sediments is adsorbed, but that igneous and metamorphic rocks

(which have been above 100 - 150°C) have very little adsorbed mercury. It is commonly thought that the form of mercury in the latter two rock-types is the sulphide (e.g. Jonasson, 1970), however this has not been demonstrated.

b. Soils

In soils mercury concentrations are similar to those in the rocks below (Aidin' yan and Troitskii, 1964; Pierce, Botbol and Learned, 1970; Jonasson, 1970 and Krenkel, 1973). Soils usually contain from 0.02 to 0.5 ppm total mercury, however in mineralised areas soils may contain over 50 ppm total mercury, including significant proportions of elemental mercury. Generally there is more mercury present in the top-soil than below (Krenkel, 1974; Frissel, Poelstra and van der Klugt, 1974). In the several Swedish soils studied by Anderson (1967), the mercury concentration varied directly with organic content.

Clays may also hold a major proportion of mercury; the mercury is adsorbed onto the clay and the amount adsorbed depends on the clay mineral. Kaolinite adsorbs little mercury, montmorillonite adsorbs mercury very strongly and is about as potent as peat and humic material (Krenkel, 1974 and this work). There are complications to any possible simple relationships because temperature, pH, the presence of other ions (e.g. Cl^-) and humic material cause changes to the adsorption/desorption of mercury. For instance a 5°C increase in temperature causes a several fold increase in the adsorption capacity of kaolinite for elemental mercury (Trost, 1970).

Some hydrous metal oxides, organic and sulphurous materials also strongly adsorb mercury (Krauskopf, 1956; Lindberg, 1973; Klusman and Landress, 1978), also Boer (1944) found that an increase in water content reduced the vaporization of mercury from soils. As yet a great deal more work is necessary before the interplay of parameters is understood, and worse, the literature contains conflicting information on adsorption (c.f. Krenkel, 1974 and 1973; Jenne, 1970 and McCarthy, Meuschke, Ficklin and Learned, 1970).

c. Sediments

The properties and concentrations of mercury in sediments are similar to those in appropriate soils. The concentration of mercury reflects the proximity of sediments to ore deposits, and the concentration processes are dominated by adsorption processes which operate similarly to those in soils. For instance top sediments in Lake Michigan show a good correlation between mercury and the organic and sulphur contents of the sediments (Lindberg, 1973). Generally mercury concentrations range from 0.02 to 1 ppm (Fleischer, 1970; Marowski and Wedepohl, 1972). A sequence

of recent sediments off California contain 0.05 to 0.16 ppm of mercury (Young, Johnson, Soutar and Isaacs, 1973), which is similar to most unpolluted sediments. Studies on mercury contamination indicate that mercury concentrations are very commonly highest in areas containing the finest grained sediments (e.g. from Bloom 1975).

The species of mercury on and in sediments is generally not known, but McNaughton and James (1974) suggest that since Hg II compounds are weakly adsorbed onto marine sediments. Andren and Harriss (1973) suggest that methyl mercury in sediments is low compared to other (inorganic) species. Hence there may be at least some limits to the type of mercury species present in certain sediments.

d. Waters

Many analyses are available for some waters, particularly estuaries, streams and geothermal waters (e.g. White, Hem and Waring, 1963; Waring, 1965: Livingstone, 1963; White and Waring, 1963; Barnes et. al, 1973; Roedder, 1972; Fleischer, 1970) and at least a few data are available for various ocean waters, lakes, groundwaters and rain; some data are given in Table (2.2). The mercury concentrations are between 10^{-5} and 5×10^{-3} ppm, with unusual waters containing up to several parts per million. Even the most polluted of natural waters contain little more than 5×10^{-3} ppm (e.g. Hosohara, Kaguma, Kawasaki and Tsuruta, 1962). High mercury concentrations are virtually restricted to subterranean waters such as brines and hot spring fluids. The Cymric oil field brines contain 0.1 - 0.4 ppm mercury and associated crude oils have up to 3 ppm (Bailey, Snavely and White, 1961). It is not uncommon for organic materials to be associated with waters at mercury deposits (Dreyer, 1940; Bailey, 1959; White, 1967), and Hem (1970) states that most mercury species are more soluble in organic solvents than water.

Of all waters, unpolluted streams probably contain the least mercury. Rain, although low in mercury, dissolves mercury from the atmosphere and apparently leaves it in the top-soil (McCarthy, Meuschke, Ficklin and Learned, 1970; Frissel, Poelstra and van der Klugt, 1974). In rivers with high mercury concentrations, most of the mercury present is adsorbed on suspended matter (e.g. Kvashnevskaya and Shablovskaya, 1963). Due to sediment settling and adsorption onto sediments waters in oceans and rivers have relatively low mercury concentrations. (Sediments nearly always contain higher mercury concentrations than the associated water; (e.g. Hinkle and Learned, 1969; Lindberg, 1973; Bloom, 1975)). Deep waters commonly have mercury contents similar to those above, except where the water lies over areas of anomalous heat flow (such as the Mid-Atlantic Ridge: Carr, Jones and Russ, 1974). Mercury in hot springs and brines range up to saturation (White, Hinkle and Barnes,

Table (2.2)

Mercury in Natural Fluids.

WATER	Concentration	References
Rain	0.05-0.5 µg/l	a
Open sea	0.03-1.2 "	a, b
Mid-Atlantic Rise	0.8-1.4 "	c
Deep sea	0.08-0.27 "	d, e
Thermal springs	<0.05-3000 "	f, g, h
Brines	6-400 "	i, j
Evaporite waters	<1-8.5 "	k
Ground waters	0.02-5 "	l, m, n
Streams and rivers	0.01-0.03 "	o, p, q
Ice (prior to 1952)	0.06 "	r
GASES		
Air - oceanic	0.6-0.7 ng/m^3	s
- continental	1-50 "	a, β, t, v
- over mercury deposits	12-1200 "	v, y, u
Soil gas - continental	<1-100 "	v, α, a
- over mercury deposits	220 "	y, u
Thermal springs/fumaroles	<5 "	u, w, x
Volcanoes	300-4000 "	v, t
Mud volcanoes	700-26000 "	u
Mine air	1-20x10^5 "	y,z

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a - Stock and Cucuel, 1934a; b - Aidin'yan, 1962; c - Carr, Jones and Russ, 1974; d - Hamaguchi, Kuroda and Hosohara, 1961; e - Hosohara, Kozuma, Kawasaki and Tsuruta, 1961; f - Ohta and Terai, 1971; g - Davey and van Moort, 1974; h - Barnes, Hinkle, Rapp, Heropoulos and Vaugh, 1973; i - Bailey, 1961; j - Skinner, White, Rose and May, 1967; k - Karasik, Goncharov, Yu and Vasilevskaya, 1965; l - Baev, 1968; m - Zautashvili, 1965; n = Wikander, 1968; o - Krainov, Volkov and Kokol'kova, 1966; p - Dall'Aglio, 1968; q - Heide, Lerz and Bohra, 1957; r - Weiss, Koide and Goldberg, 1971; s - Williston, 1968; t - Eshleman, Siegel and Siegel, 1971; u - Aidin'tan and Ozerova, 1966; v - Barber, Beauford and Shieh, 1973; w - Davey, 1974; x - White, 1967; y - Sergeev, 1961; z - Neville, 1967; α - McCarty, Meuschke, Ficklin and Learned, 1970; β - Stock and Cucuel, 1934b.

1970; Davey and van Moort, 1974; Davey, 1974) and is known to condense from fluids at Yellowstone National Park (White, Hinkle and Barnes, 1970), the Cymric Oil Field (Bailey, Snavely and White, 1961; White, 1967) and at Ngawha Springs, (this work).

Generally when mercury is high in natural waters, the concentration has decreased to near background levels by a few tens of kilometres via sedimentation, sorption and complexation reactions with clays, plankton, colloidal proteins, humic materials and other inorganic and organic colloids (Wershaw, 1970; Hem, 1970; Hoggins and Brooks, 1973).

e. Air

Mercury is present in the atmosphere in very low but detectable concentrations which vary greatly with weather and location; for instance the air has higher mercury concentrations over landmasses than seas (McCarthy, Meuschke, Ficklin and Learned, 1970), and is a large reservoir of mobile mercury as well as a major supplier of 'anomalous' top-soil mercury (Gavis and Ferguson, 1972; Kothny, 1973; Frissell, Poelstra and van der Klugt, 1974). Relatively few accurate determinations of mercury in unpolluted air have been made. Some of the available data are 0.02 $\mu g/m^3$ (Eshelman, Siegel and Sigel, 1971; Siegel, Siegel, Eshelman and Bachmann, 1973), 0.003 - 0.01 $\mu g/m^3$ (McCarthy, Mueschke, Ficklin and Learned, 1970), 0.2 $\mu g/m^3$ (Gavis and Ferguson, 1972), 0.0006 $\mu g/m^3$ (ocean air, Williston, 1968), 0.035 $\mu g/m^3$ (Hobart, Tasmania in 1976). Air in mineralised areas contained 0.20 $\mu g/m^3$ (Barber, Beauford and Shieh, 1974) and 1.2 $\mu g/m^3$ (Aidin'yan and Ozerova, 1966). Wind thus may cause considerable variation in local mercury concentrations; e.g. winds off an oceanic area cause low concentrations, whereas those from continental areas of mineralisation give rise to high levels of mercury in the air. Down-wind from volcanoes higher mercury levels have also been recorded (Eshelman, Siegel and Siegel 1971; Siegel, Siegel, Eshelman and Bachman, 1973).

Mercury concentrations also depend on diurnal changes (e.g. 0.02 - 0.6 $\mu g/m^3$), barometric pressure, altitude and rain (McCarthy, Mueschke, Ficklin and Learned, 1970). After a rainstorm atmospheric mercury levels have been known to drop below detectable ($\leqslant 0.001\ \mu g/m^3$).

The main forms of mercury in air are probably elemental mercury, minor organomercurials (from plant and animal decay) and mercury on particulate matter.

f. Gases

Fumarole and soil-gas mercury concentrations range more widely than those in air: from undetectable ($< 0.5\ \mu g/m^3$) to about $7.5 \times 10^8\ \mu g/m^3$ (Tables (2.2) and (A.12)). A striking example of mercury in gas is the estimated hundreds of tonnes of mercury condensed from the Cymric Oil Field gases! (White, Hinkle and Barnes, 1970). The highest analysed mercury concentrations occur at mercury depositing springs (see data in White, 1967; Fliescher, 1970; Davey, 1974); e.g. 130 ppm Hg in steam at the Geysers from which cinnabar is deposited. Mercury has been detected in many hot spring gases (Aidin'yan and Ozerova, 1966; Dickson and Tunell, 1968; Barnes, et al, 1973), and volcanic emanations may contain considerable mercury also; e.g. $\geqslant 2.5 \times 10^4\ \mu g/m^3$ (Aidin'yan, 1966; Eshelman, Siegel and Siegel, 1971; White and Waring, 1963; Siegel, Siegel, Eshelman and Bachmann, 1973).

Soil-gases usually have much higher mercury concentrations than the air above, although mercury diffuses into the air to cause anomalous concentrations which can be used for the detection of ore deposits (McCarthy, Vaughn, Learned and Meuschke, 1969; Barringer, 1972; Ozerova, 1973; Krenkel, 1974). Above and about ore deposits, soil-gases (and air) have the highest mercury concentrations (Sergeev, 1961). However areas mineralized at high temperatures may have negative mercury anomalies (Hoggins, 1972).

Below the top-soil in unmineralised areas it is postulated that mercury in soil gas is lower (Krenkel, 1973). The higher mercury in the top-soil is believed to be due to adsorption of mercury from rain and the affinity of the organic matter for mercury (Anderson, 1967; Frissel, Poelstra and van der Klugt, 1974). However Jenne (1970) believes that soil mercury originates from below and diffuses up into the atmosphere. (This is a possible explanation for the higher concentrations of mercury over land-masses than over oceans, the high mercury concentrations in soil gases over mercury deposits and why mercury in soil gases is several orders below saturation even where the under-lying rocks have very high mercury concentrations. An alternate explanation for the low mercury levels over oceanic areas is that mercury dissolved in the water is dispersed more rapidly by currents and is eventually adsorbed onto sediments and lost from the atmosphere to the bottom of the sea). The high anomalous concentrations of mercury in soil-gas over mineralized areas shows that mercury can originate from below the soil. Data of Ehmann and Lovering (1967) indicate that deep rocks contain higher concentrations of mercury than shallow crustal rocks, which may mean that mercury permeates into the air directly from the crust.

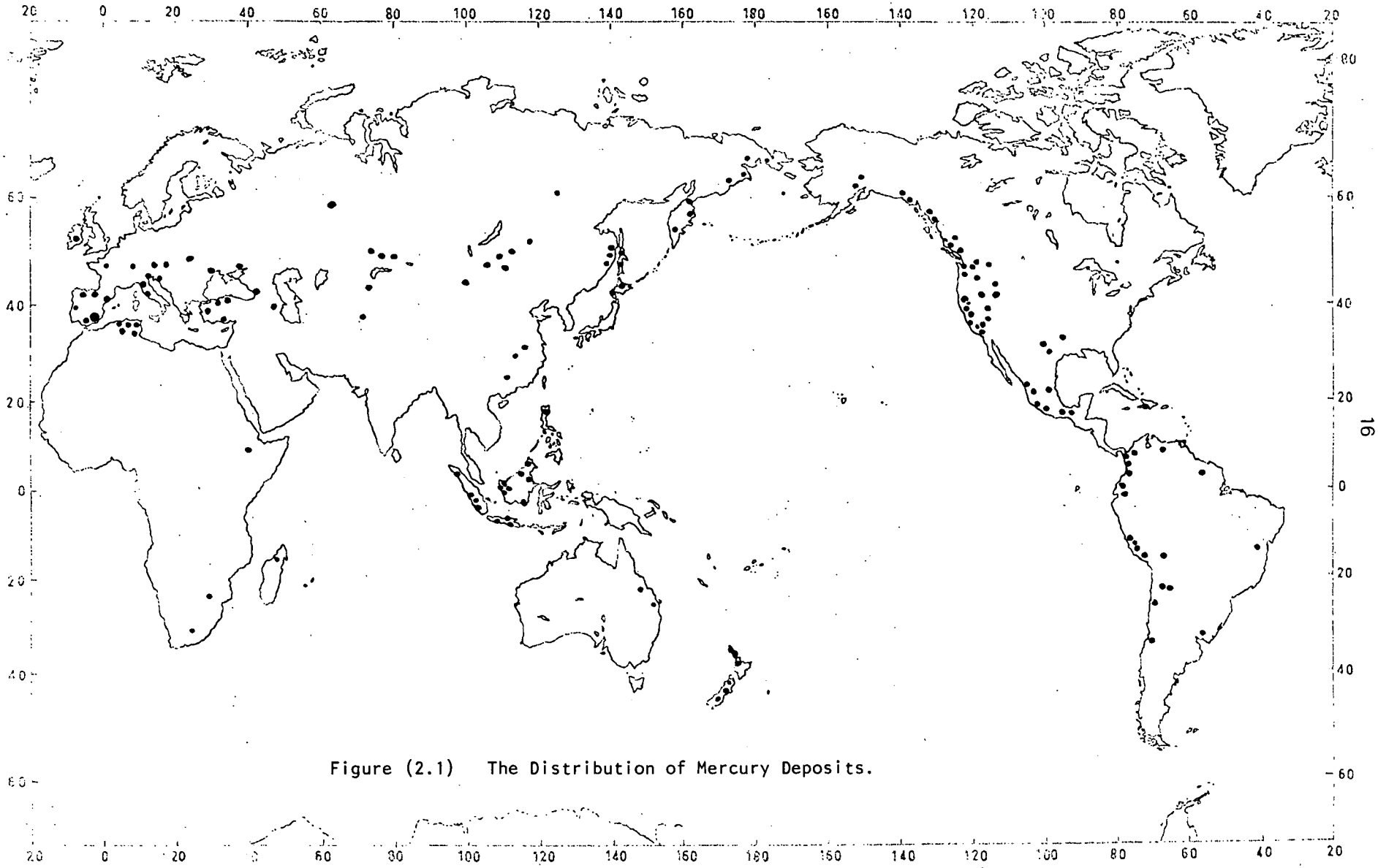


Figure (2.1) The Distribution of Mercury Deposits.

The above discussions show that the mercury vapour pressure in soils depends on the moisture content, the atmospheric conditions, the organic content, geothermal activity, and the amount of mercury present in the country rocks. Where rocks are not high in mercury and are not in a geothermal system, it seems unreasonable to expect that any significant mercury can come from below. The high mercury concentrations in continental air is probably due to recycled biospheric mercury caused by decay, desorption, degassing in low pressure weather and pyrolysis and photolysis due to radiation from the sun; (photolysis was observed at Ngawha Springs). The fact that mercury is mostly trapped in the top-soil where it is easily lost to the atmosphere suggests 'cycling' between soil, air and rain, which is restricted in the sea due to water currents and sediment adsorption which can remove a significant proportion of the mercury from the cycle.

In summary the available analyses for mercury in gases suggest an enormous range exists, and that there is possibly no ambient, not even locally. The most stable concentrations would be in very low rainfall climates either over mid-ocean or mid-continent.

(2.3) MERCURY DEPOSITS

Mercury deposits are readily characterised from other deposits and have many parameters in common (Dreyer, 1940; Ross, 1942; White, 1967; Moiseyev, 1971; Fedorchuk, 1974). For instance the distribution of mercury deposits is shown in Figure (2.1), and Figures (2.2) and (2.3) show the distribution of hot springs (mostly from Waring, 1965) and known emissions of elemental mercury respectively; the location of crustal plate boundaries appear in Figure (2.4). The correlation of mercury occurrences, hot springs and plate margins is thus obvious, however the correlations are not unique to mercury deposits. Listed below are the significant features of mercury deposits, many of which are characteristic (and designated *).

a. Characteristics

* 1. Deposits are commonly associated with fluids which are dilute brines (White, 1967; Barnes et al, 1973; Roedder, 1972 and 1975 and Fedorchuk 1963; Maslova, 1963 and Table (2.3)).

* 2. Deposits and emanations are usually within a few hundred kilometres of plate boundaries active at sometime since the Palaeozoic (Figures (2.1) and (2.4)).

* 3. Few deposits are pre-Cretaceous (Moiseyev, 1971).

* 4. No deep deposits are known: the deepest is New Almaden at 360 m (Bailey and Everhart, 1964), most deposits are less than 200 m deep.

* 5. Where information is available, deposits and deposition occur in areas of high surface temperatures (White, 1967) and very steep thermal gradients (e.g. White and Roberson, 1962; Banwell, 1966).

* 6. Large amounts of CO_2 - rich gas and/or water are frequently present (Fedorchuk, 1963; White, 1967; Barnes et al, 1973 and 1975 and Roedder 1962 and 1975).

7. There is no correlation between mercury content and sulphur content of ore-fluids (White, 1967; see also data in Barnes, 1970 and Barnes et al, 1973). Most springs and inclusions contain between 0.1 ppm and 30 ppm total reduced sulphur. The total range is from less than 0.1 ppm to 180 ppm; very few springs contain more than 30 ppm.

8. Relatively high concentrations of boron and ammonia are associated with mercury bearing springs, especially in the circumpacific belt (White, 1967; Roedder, 1972) however there is no apparent correlation between the concentration of these species, or any others, and mercury concentration.

9. Mercury concentrations in waters lie between less than 0.0001 ppm and 2.3 ppm (from data in White, 1967; White, Hinkle and Barnes, 1970; Ohta and Terai, 1971; Roedder, 1972; Barnes et al, 1973; Dall'Aglio, 1968; Davey and van Moort, 1974).

* 10. Mercury is present in the hot spring gases and ranges from just detectable ($\leqslant$ 1 μg/l) to nearly 800 μg/l (4 μM/l) (Aidin'yan and Ozerova, 1966; Dickson and Tunell, 1968; White, 1967; White Hinkle and Barnes, 1970; Davey and van Moort, 1974; and Davey, 1974). The mercury is elemental where determined.

* 11. pH is usually in the range 5.0 to 8.5 where mercury is depositing as cinnabar (Fedorchuk, 1963; White, 1967; Barnes et al, 1973; White, Hem and Waring, 1963, Ellis and Mahon, 1966). The rare extreme pH's lie in the range of 1 to 12 units.

* 12. Organic material (oil, tar, methane) is commonly associated (White and Roberson, 1962; White, 1967; Bailey, 1959; Davey, 1977).

* 13. Deposition temperatures lie between 30° and 200° C (Dreyer, 1940; Thompson, 1954; Ozerova, 1962; White, 1967; Roedder, 1972; Davey and van Moort, 1974; Davey, 1977).

* 14. Deposition pressures are commonly below 30 atmospheres. (Dreyer, 1940; Ozerova, 1962; Dickson, 1964; White, 1967; Moiseyev, 1971; Davey, 1974 and 1976).

* 15. Deposits have broad haloes of anomalously high mercury concentrations (Ozerova, 1962 and 1973; Figure (8.2) this thesis).

* 16. Cinnabar is usually the only mercury mineral present in economic quantities, other mercury minerals are rare or not present (Dreyer, 1940; White, 1967). The most common other forms of mercury possibly present are elemental mercury and seldom metacinnabar.

* 17. Rarely is more than one other metal sulphide mineral present in significant quantities (Dreyer, 1940). Other sulphides present may be of iron, antimony or arsenic. A large number of deposits contain only cinnabar plus gangue minerals such as quartz or other silica minerals, carbonates or/and sulphates (Moiseyev, 1971; Maslova, 1963).

* 18. Very few mercury deposits contain more than 5,000 tonnes of economically to subeconomically recoverable mercury (Moiseyev, 1971). Only about five deposits appreciably exceed this. The largest is Almaden (Spain) which had a little more than 700,000 tonnes before mining (Saupé, 1976).

19. Mercury deposits are associated with a large variety of host and wall rocks (Dreyer, 1940). In a given locality there may be a preference for a given rock-type host. Generally where mercury deposits, the host is either porous or easily altered to penetrable by the ore-solutions. In other cases mercury deposits directly from the flowing springs as they emerge at the surface. (Wall rocks may not react with the solution, and where they confine host materials there is usually an abrupt fall in mercury deposition.)

20. Moiseyev (1971) states that 65% of all mercury deposits are associable with various volcanics (no preferred type). However deposits are more associable with sediments (either modern or at the time of deposition), and all but 10 to 15% of deposits are associated with sediments. (Several important deposits are associable with highly brecciated sediments (e.g. Franciscan Formation) or other sediment piles). Very few deposits can be associated with metamorphic terrains above greenschist facies (ca. 10%) (Moiseyev, 1971).

* 21. There are no submarine-formed cinnabar deposits.

Few mercury deposits depart from the above characteristics although some deposits may not fit one or two of the listed points. The above points are empirical, hence a discussion is unwarranted until the mechanisms for mercury deposition are developed. However the above observations concerning mercury deposits suggest that a study of hot springs depositing cinnabar is pertinent to all the deposits.

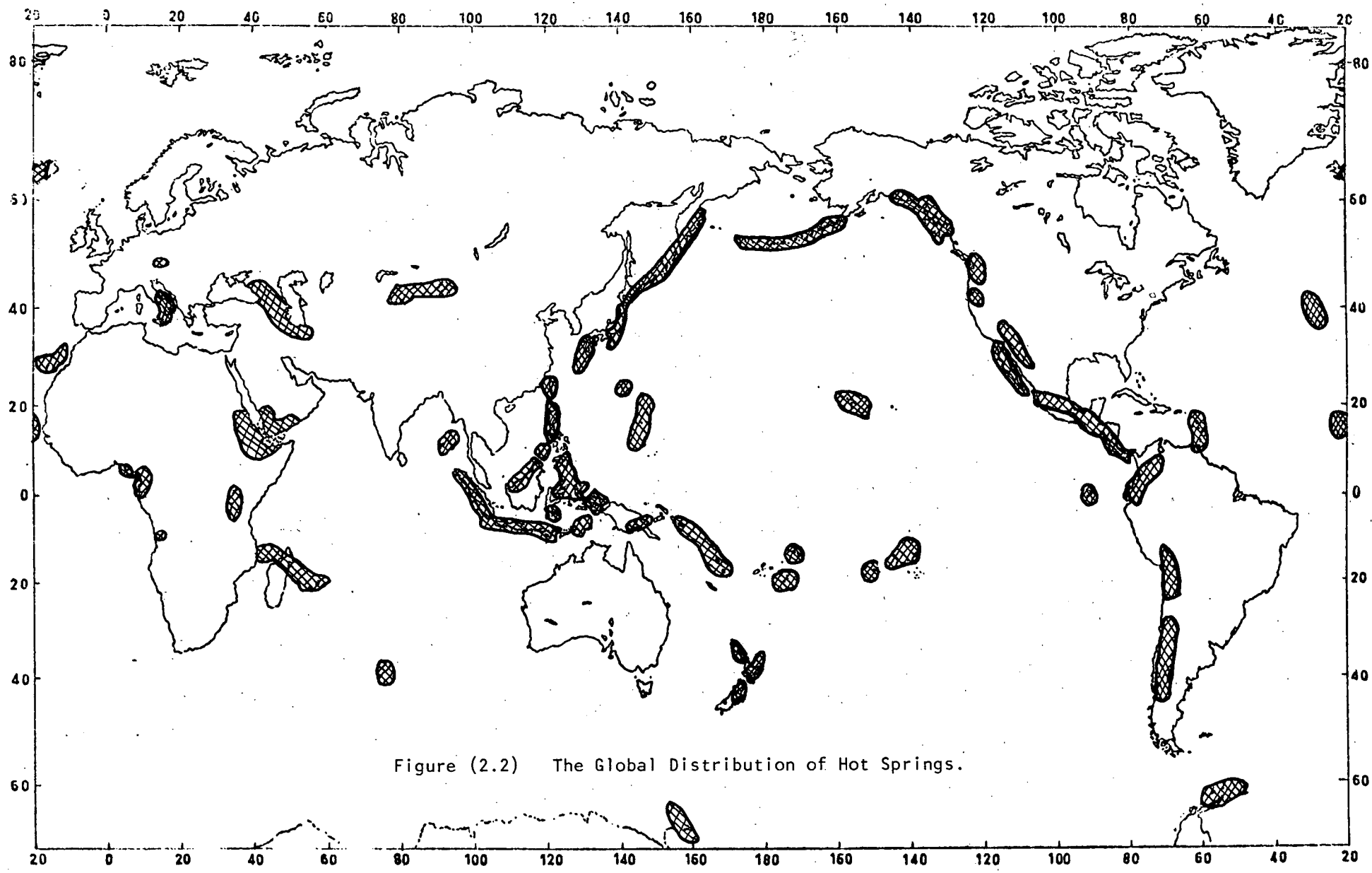


Figure (2.2) The Global Distribution of Hot Springs.

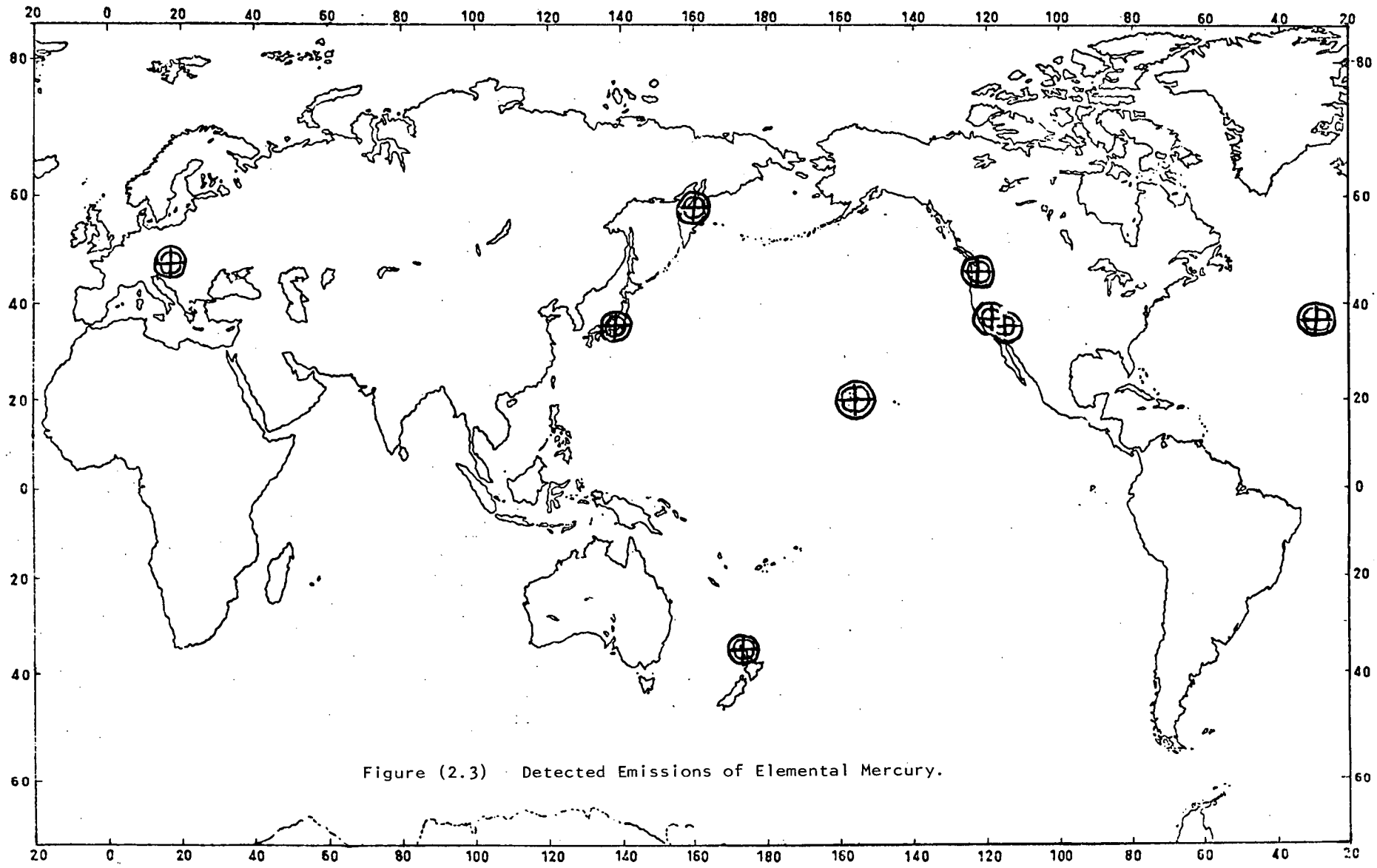


Figure (2.3) Detected Emissions of Elemental Mercury.

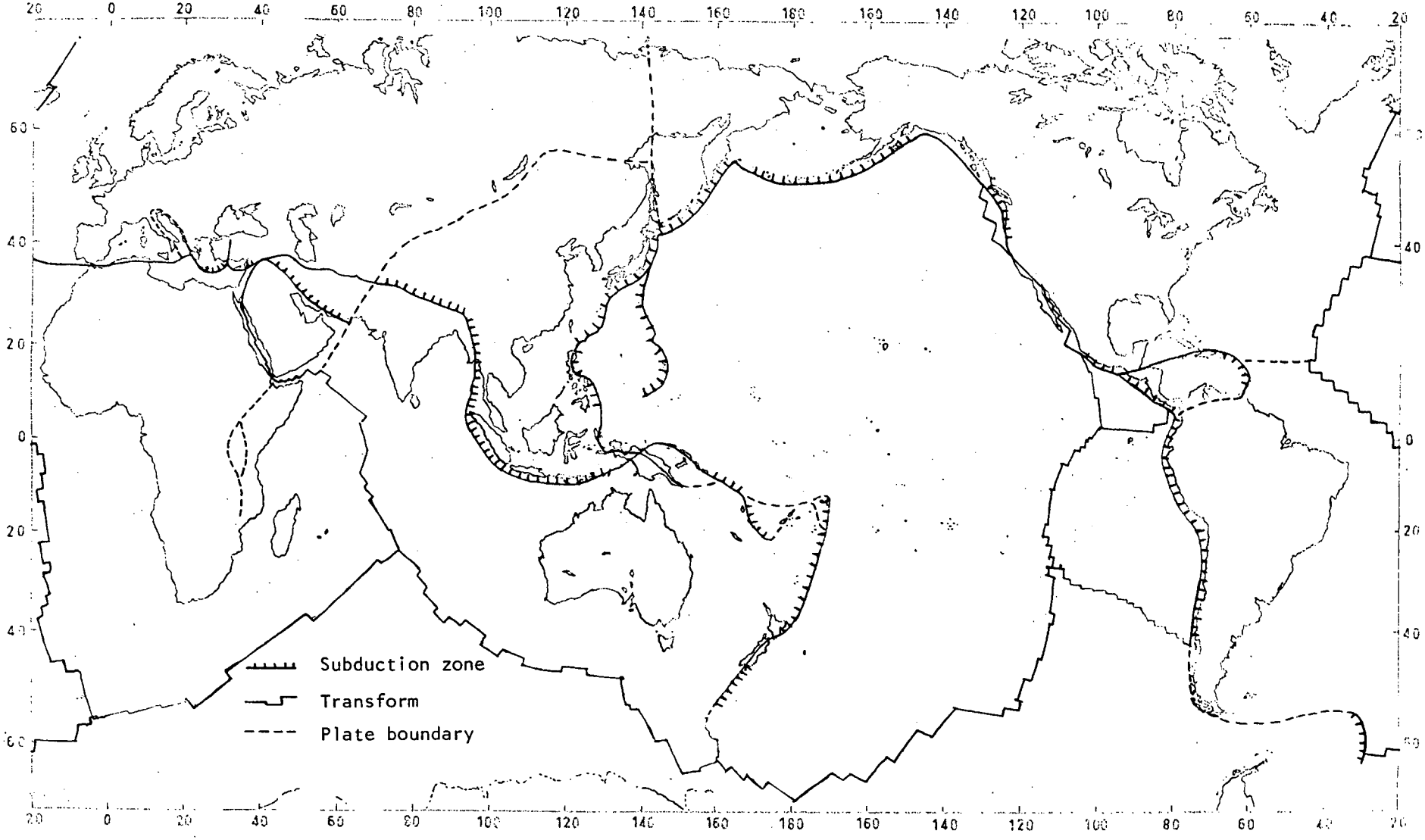


Figure (2.4) Tectonic Plate Margins.

TABLE (2.3) Analyses of Fluids Associated with Cinnabar Deposition (ppm)

Location	Temp.	pH	K	Na	NH_3	Fe	Hg	Cl^-	$\Sigma SO_4^=$	$\Sigma S^=$	ΣHBO_2^-	ΣHCO_3^-	ΣSiO_2	References
Wilbur Springs	55°	6.9	440	8500	280	0.04	0.0015	9700	390	190	1550	7130	200	f, n
Kamchatka	170°	8.9	940		0.7	-	-	1470	164	-	155	86	170	e
Sulphur Banks	85°	7.95	41	1310	490	0.38	0.002	782	1630	4	3100	2100	140	f, g
Tamagawa	98°	1.2	65	114	-	105	0.01	3240	1330	-	115	-	324	h, i
Boiling Springs	88°	9.2	1.9	74	-	0.4	⩽.01	14	12	< 1	0.5	106	0.1	h, f
Okahi	95°	7.0	82	860	3.8	-	2000 in sediments	1060	100	1	130	490	338	j
Steamboat	93°	7.5	60	605	< 1	<0.01	present	820	123	present	160	330	220	o, p
Jubilee (Ngawha 1976)	90°	5.8	64	740	109	<0.1	0.3	1040	290	10	2900	533	135	a, b, c
Jubilee (1963)	49°	6.9	79	870	8	-	-	1336	500	-	4140	310	186	d
NG1	230°	7.4	80	950	46	0.1	⩾0.5	1625	17	present	4862	85	460	e, d
Fluid Inclusions														
Pacific 'USSR'	-	-	380	1300	-	-	-	660	-	(trace (0.01	-	1510	-	k
"	-	-	40	140	-	-	-	40	-	-	-	320	-	k
Kamchatka	-	6.74	105	1315	-	-	-	600	-	⩽0.01	-	1500	-	l
Alaska	-	-	-	-	-	-	solid present	-	-	-	-	saturated + liquid CO_2	-	m

References:- a = Barnes in b = Giggenbach and Lyon (1977); c = Davey and van Moort (1974); d = Ellis and Mahon (1966); e = Ellis (1970); f = Barnes (1973); g = White and Roberson (1962); h = White (1967); i = Ohta and Terai (1971); j = Weissberg (1969); k = Maslova (1963); l = Fedorchuk (1963); m = Roedder (1962 and 1972); n = White, Barnes and O'Neil (1973); o = White (1968); p = Dickson and Tunell (1968).

b. Fluids and Mercury Deposition

Because geothermal fluids are associated with all known mercury deposits (e.g. White, 1967; Roedder, 1972; Barnes et al, 1973; Figures (2.1) and (2.2)) a major consideration in the deposition of cinnabar is the processes involving geothermal fluids. Hence a review of mercury depositing environments is essential for comparison with Ngawha Springs.

The data on hot springs (Table (2.3)) demonstrate that the Ngawha Springs are not of unusual composition or geological environment for mercury depositing springs. This means that processes occurring at Ngawha Springs may be applicable elsewhere, and possibly to all mercury deposits.

The fluid composition data in Maslova (1963), White (1967), Ellis (1970), Fleischer (1970), Ellis and Mahon (1966), Barnes et al (1973), Roedder (1972) and Giggenbach and Lyon (1977) show that spring chemistry is variable and hence a detailed discussion is useless. All the relevant data has been included in the previous section on characteristics. General spring chemistry has also been discussed by White (1967), and similar compositions are found in fluid inclusions (Maslova, 1963; Fedorchuk, 1963; Fedorchuk, Kostyleva and Maslova, 1963; Tender, 1967; Bannikova, Sushchevskaya and Volkov, 1975). The important aspects of spring chemistry as regards mercury deposition and transport are developed in the following section about the mechanisms involved.

(2.4) MERCURY DEPOSITION

Deposition involves a three stage process:-

1. Mobilization from a source.
2. Transport from source to deposit and
3. Fixing (Precipitation) of the mobile species (deposition itself).

Few studies have been made on the first and last stages, and even fewer investigations of any of the stages have been made on hot spring systems. Most work has been confined to laboratory systems. Three transport and fixing processes are known to occur in nature (Davey, 1974, 1977 and in this thesis), although many suggestions have been presented in the literature (Krauskopf, 1951; White, 1967). In fact, of about 45 spring areas associated with recent cinnabar deposition, about ten are known to be depositing cinnabar, yet only one area has had any deposition processes and mechanisms determined.

a. Mobilization

Relatively little attention has been given to how mercury is mobilized from a source. Chemistry indicates that mercury may be released by:-

1. Pyrolysis or
2. Leaching.

The ease and efficiency of mobilization also depend on the form of mercury, concentration, temperature and access to the transport medium. Mercury may be bound physically (e.g. adsorbed), chemically or structurally onto and/or into the source: thus the nature of the mercury in the source greatly influences mobilization and may even prevent it.

1. Pyrolysis.

A fairly characteristic temperature range for complete or nearly complete liberation of each kind of bound mercury in a rock exists (Fedorchuk, 1961; Ozerova, 1962; Koksoy and Bradshaw, 1967; Bradshaw and Koksoy, 1968). Adsorbed mercury is mostly released by 250 to 300° C depending on the chemical form adsorbed. Elemental mercury may be completely released at temperatures as low as 120°, but compounds require higher temperatures. The sulphide and oxide require the highest temperatures and in the extreme, the oxide may require temperatures of almost 450° for complete release (Bradshaw and Koksoy, 1968).

Mercury in common rock-forming silicate mineral lattices requires a similar range of temperatures for release, though not as high as for the adsorbed oxide. (Ozerova, 1962; Bradshaw and Koksoy, 1968). The temperature range is 150° to 400° C with some less common minerals requiring almost 500° C.

Most strongly bound is mercury in other sulphide minerals: Sulphides stable to over 700° C require 700 - 750° C to release most of the mercury (Ozerova, 1962). (It should be noted that a small partial dissociation under laboratory time interals and conditions could be highly significant in geological situations, and hence reduce the effective mobilization temperatures by a few tens of degrees).

The most important consequence of the pyrolysis of possible sources is that mercury is released as the element. Hence it may move as the vapour from the source (and it is stable). All known feasible chemical compounds (and complexes) are dissociated by 500° C, and considerably less if a mobile vapour phase is present, ca. 250° C (cf. Krauskopf, 1951; White, 1967; Hem, 1970).

2. Leaching.

Very little has been published on the leaching of mercury under geological conditions. Leaching experiments have mostly concentrated on other elements

(Dickson, 1976). However, since mercury deposition is associable with anomalously high temperatures (White, 1967), then as the hot fluids 'digest' a mineral or rock and access the mercury, the temperature is commonly high enough to remove mercury without, or before, significant leaching of mercury occurs. The view is strongly supported by experimental evidence of the author and Dickson (1968 and 1964), because above 200° C in closed systems all feasible mercury solutions start to decompose significantly and the decomposition is more pronounced in open systems.

Leaching experiments with dilute brines ($\leqslant$ 1.5% Cl^-), spring waters and rocks from Ngawha Springs showed that temperature was more effective in extracting mercury than chemical dissolution. (Rocks include basalts, andesite, limestones, pelitic and siliceous shales and clays). The rocks had been crushed to promote solution penetration and left for up to three years. At relatively low temperatures 80 - 125° C, which reduce mercury pyrolysis, mercury was still extracted into solution slowly, and the presence of a mercury 'getter' out of contact with the solution and rock, and only contactable by vapours, took up most of the mercury, left little in solution and less in the rock. The escape of mercury thus enhances the attack of the leaching agent. Conversely leaching agents (especially Cl^-) may enhance the escape of mercury. Above ca. 120° C there is a considerable increase in mobilization due to the presence of a dilute brine.

The low temperature runs removed significant amounts of mercury during the entire time (three years), but in most cases did not remove more than 40 - 70% of the total mercury. The concentration of CO_2 did not appear to be very significant to the extraction of mercury. However the presence of chloride was essential at the low temperatures, without more than a few parts per million, very little extraction occurred. At high temperatures it enhances extraction, and does not appear to be essential above about 300° C if mercury can escape.

It is probable that at temperatures between 100 - 150° C that a combination of initial leaching then pyrolysis/dissociation may occur via:-

1. Attack of rock and mercury dissolution.
2. Partial dissociation of mercury complex/salt to element.
3. Escape of dissociated element via vapour in gas phase.

In summary the initial leaching process is more effective below ca. 200° C, and pyrolysis is more effective above ca. 300° C (and in some instances at lower temperatures). In either case at temperatures above 100° C mercury moves from the solution into the vapour phase. Below ca. 100° little mercury is mobilized from most rocks, except the adsorbed element.

Since mercury deposits between ca. 30° and 200°C, then in nature most mercury would be mobilized at temperatures well in excess of 200°. Therefore pyrolysis (with a probable fluid intermediate) is favoured.

Mobilization via complexation is inferred (though not stated per se) by many authors who favour the transport of mercury as complexes of reduced sulphur species (Schwarzenbach and Widmer, 1963; Dickson, 1964; Barnes, Romberger and Stemprok, 1967; Dickson and Tunell, 1968). The process requires solution attack of a rock before the mercury is released as presumed cinnabar (since this was used in all the experiments as the starting material)! However at the temperatures desired for the assumed direct complexation ($>$ 200°C) considerable decomposition of the complexes occurs (Dickson, 1968). Moreover direct complexation is only likely when Hg II is released during leaching and not pyrolysis. Hence the 'alkaline sulphide hypothesis' is restricted to temperatures well below 300°C, as discussed above, and well below 250° in open systems with gas judging from Dickson's experiments in a closed system. Thus normal subterranean conditions (data on the deep drill-holes in Ellis and Mahon (1966), White (1967) and Ellis (1970) and the steep thermal gradients) would severely restrict the mobilzation zone to relatively shallow depths, hence there could be insufficient source material to yield a significant quantity of mercury. Pyrolysis yields Hg^{o} (e.g. Bradshaw and Koksoy, 1968) which does not complex with any known natural geothermal spring species (unless a strong oxidizing agent is present). However Hg^{o} is more than sufficiently soluble in natural waters to allow transport and ore formation (Davey, 1974 and 1977). Commonly there is insufficient organic material present to transport mercury to form a deposit.

Experiments using a variety of pH's and sulphide concentrations on mercury and mercury compounds demonstrated that although some mercury compounds could dissolve slightly, that for the composition ranges of the springs and waters at Ngawha Springs, that elemental mercury was by far the most soluble species. In order to dissolve elemental mercury as sulphide complexes, it was found that a trace of oxygen (or air) was needed, and at low temperatures solid cinnabar was obtained, however the presence of a sufficient and continuous supply of oxygen in most hot spring areas in the mobilization region is very unlikely. (No runs to obtain cinnabar were carried out above 35°C).

In summary mercury is most likely mobilized by pyrolysis which yields the free element, (which favours vapour phase transport).

b. Transport

The consideration of species involved in mercury transport by ore-solutions dates back to Knox (1906), who found that cinnabar may be dissolved in aqueous

sodium sulphide solutions. Since then, a number of authors have made laboratory studies of the H_2S - Na_2S - HgS - H_2O system (Dickson, 1964 and 1968; Schwarzenbach and Widmer, 1963; Barnes, Romberger and Stemprok, 1967; Khodakovsky, Povova and Ozerova, 1975). Krauskopf (1951) considered a variety of possible mechanisms for transport and concluded that the dissolution of cinnabar as sulphide complexes was the most feasible of the proposed mechanisms. However no natural system has yet been demonstrated to transport mercury as any combination of reduced sulphur complexes, moreover many hot springs contain too much mercury to be accounted for by sulphide complexation.

In 1974 Davey showed that cinnabar deposits from elemental mercury in mixing waters at Ngawha Springs, and later he found a species of sulphate reducing bacteria which also cause the deposition of cinnabar (Davey, 1977).

Most attention has been given to this stage of the deposition process and in spite of several suggested mechanisms, few have been shown to occur naturally. The review of possible mechanisms made by Krauskopf (1951) concludes that of nine possible transport mechanisms, plus the two mentioned at the end of the paper, that only three were probable:-

1. Alkaline sulphide complexes,
2. Volatile chloride ($HgCl_2$) and
3. Elemental vapour.

Of the above suggestions, the only one known to transport mercury in nature is the last (Davey and van Moort, 1974 and Davey, 1974). In addition to the above observed mechanism, three others have also been observed:-

4. Aqueous mercury metal,
5. Aqueous mercury II and
6. Organo-mercury vapours.

All latter three mechanisms occur at Ngawha Springs, however the fifth and sixth mechanisms are responsible for only minor mercury transport. The Hg II species is formed by the mixing of the element in springs fluids with oxidizing surface waters. Cinnabar is deposited from the reaction of the Hg II and H_2S. The organo-mercurial was found by infrared spectroscopy of gas condensates (ca. - 5° to 10°C) from the Tiger Bath at Ngawha Springs. The organic structure inferred contains '-  - Hg - S -', a phenyl mercury sulphur linkage, and forms about 0.1% or less of the mercury evolved in the gas emission.

The mechanisms 1 to 4 are able to transport sufficient mercury in the right circumstances, but there are several problems with the first two mechanisms which severely limit their likelihood. The geochemical experiments and calculations on the solubility and stability of cinnabar in alkaline sulphide solutions (Knox, 1906; Dickson and Tunell, 1968; Schwarzenbach and Widmer, 1963; Dickson,1964, 1976 and 1968; Barnes, Romberger and Stemprok, 1967; Barnes and Czamanske, 1967 and Khodakovsky, Popova and Ozerova, 1975) have been carried out on the dissolution of cinnabar and metacinnabar in closed systems, which are heated up from cold and have irreversable decomposition at moderate temperatures (ca. 200° C). The second suggested transport possibility has not been taken very seriously, little work has been done on it and a mere comment occurs in some literature. Consideration of the behaviour of $HgCl_2$ at high temperatures in chemical systems suggests that it is rarely an important mode of transport. On the other hand aqueous mercury - chloride complexes are more feasible.

The Alkaline Sulphide Hypothesis or Mechanism 1.

The basic problems are:-

a. Thermal instability above 200°,
b. HgS is an unlikely major form of mobilized mercury,
c. Required pH's are too alkaline in most cases,
d. $\Sigma\ S^{=}$ required is too high,
e. Unfavourable Eh/pH conditions and
f. Probable reaction with Fe^{2+}.

a. Dickson's experimental data on the HgS - Na_2S - H_2S - H_2O system (1964) and later comments (1968) show that significant thermal decomposition (ca. 30%) takes place between 200 and 250° C. In nature the solutions would not and could not be formed by heating cold cinnabar in cold Na_2S - H_2S solutions (which also have more sulphide than any analysed spring), for the mobilized mercury species move into solutions hotter than those investigated by Dickson. (As mentioned earlier mercury is deposited from solutions in the temperature range 30 to 200° C, and it is generally conceded that the solutions are hotter prior to deposition).

During Dickson's experiments drops of liquid mercury formed (1968, p. 363) from the dissolved cinnabar complex and the reaction was not reversible with cooling. Since the proposed complexes would have to form in an open system at temperatures above their dissociation/decomposition range in a closed system, only the element would result, and on cooling no complex would form.

b. All the workers (listed four paragraphs back) have directly used cinnabar to make their solutions; i.e. they have assumed cinnabar is mobilized from the source and is therefore stable at the mobilization temperatures. However as discussed earlier the cinnabar is dissociated by 300°C or less. In the presence of a moving gas or supercritical fluid phase significant dissociation occurs at much lower temperatures, and eventually all the cinnabar (or other mercury compounds) is dissociated and escapes as the element (Krauskopf, 1951 and 1956; White, 1967; Hem, 1970). Normally a CO_2- rich gas phase is associated with mercury-deposition fluids (White, 1967) and thus enhances the dissociation of any possibly formed sulphide complex: a contrast to the closed system used by Dickson. With regard to the possible formation of the complex below 200°C, the most common form of source mercury in rocks does not appear to be cinnabar but adsorbed mercury of other kinds, including the element (discussed earlier from Koksoy and Bradshaw, 1967; Bradshaw and Koksoy, 1968; Ozerova, 1962 and Moiseyev, 1971).

c. & d. The solubility of mercury - sulphide complexes is very low unless pH's exceed 10, or about three units alkaline (Barnes, Romberger and Stemprok, 1967) The other critical factor is the reduced-sulphur concentration of the springs and fluid inclusions; it rarely exceeds 10^{-3}M, which for pH's of 7, 8 and 10 correspond to mercury solubilities of about 5×10^{-5}, 10^{-4} and 7×10^{-2} ppm respectively. Most spring waters have near neutral pH's (White, 1967; Barnes, et al, 1973; Tunell, 1964) and therefore could hold up to 10^{-4} ppm total mercury (calculated from Barnes, Romberger and Stemprok). This is too low to produce the mercury concentrations detected (White, 1967 and 1970; Ohta and Terai, 1971; Barnes, et al, 1973; Davey and van Moort, 1974) or form a mercury deposit. Assuming 100% deposition,1 tonne of cinnabar would require at least 10^{13} litres of solution, an excessive quantity of liquid (e.g. Krauskopf, 1951).

e. All commonly feasible mercury II (and I) ions, compounds and complexes are not favoured by the redox conditions usually present in hydrothermal systems. Considitions lie between pH 5 to 10 and E_h + 0.6 to -0.45 volts (from data in Hem, 1970; Parks, 1971 and Weast, 1976), and the E_h range contracts to below + 0.3 where no contact with oxidizing waters occurs. This limits the stability fields of mercury in deposition fluids to elemental mercury, cinnabar and mercury sulphide complexes (per Schmitt, 1962; Garrels and Christ, 1965; White, 1967; Krauskopf, 1967; Hem, 1970). From the discussion on the thermal instability of cinnabar and sulphur complexes, the presence of feasible mercury compounds above ca. 250°C is thus prohibited, and the element is the only stable form of mercury expected in most geothermal systems.

f. Ferrous iron (Fe^{2+}) which is commonly present in geothermal solutions and is more abundant in rocks, can react with mercury according to the following equation:

$$Hg^{2+} + 2Fe^{2+} \rightarrow Hg^{o} \nearrow + 2Fe^{3+}$$

The reaction is kinetically and thermodynamically favoured, and again mercury is produced as the mobile element. The relatively common presence of iron in spring waters (White, Hem and Waring, 1963; Waring, 1965; Ellis, 1970; Barnes, et al, 1973) is indicated by the fact that iron forms one of the very few other sulphides present at many cinnabar deposits (Dreyer, 1940; White, 1967). As mentioned previously mercury partitions into the gas phase (if present), and relatively little accompanies the liquid phase, which holds the iron).

In summary of the alkaline sulphide hypothesis, it is probable that the various complexes can only be formed and exist for useful time intervals below 180° C in most hydrothermal systems, provided Fe II is absent or very low in concentration. The absence of a gas phase may increase the stability range of the complexes to little more than 200° C at best.

General dissatisfaction with the alkaline sulphide hypothesis has been expressed by several authors who believe that the required solutions should resemble those found in nature (Yates and Thompson, 1949; White, 1967; Krauskopf, 1951 and 1976; Davey, 1974).

The Volatile Chloride Mechanism.

From the above arguments the transport of mercury as the undissociated vapour (or chloride complexes) is unlikely; e.g. $HgCl_2$ is dissociated appreciably at 120° C (Weast, 1976; Perry, 1963), and nearly an 100% mercury recovery can be obtained from it near 200° C (Bradshaw and Koksoy, 1968). The dissociated chlorine is hydrophilic and therefore tends to go into solution whilst mercury favours the gas phase. Hence the presence of gas and liquid phases enhances the separation of mercury and chlorine above 120° and hence mercury vapour is transported. Another problem is that chlorine is very reactive and attacks rock and some solution species. Few rocks are unreactive to chlorine, so the chlorine is irreversibly lost. (The improbable presence of excess chlorine would enhance the possibility of the mechanism occurring.)

Generally the mechanism is not feasible except for dry gases; volcanic gases are a possibility. Sublimed $HgCl_2$ would form, and some may convert to HgS if H_2S

is present. The absence of an aqueous phase inhibits mercury deposition apart from sublimation, for losses to the atmosphere could be large unless the vapours are suddenly chilled and are able to deposit the sublimate.

Complex chlorides of mercury have not been closely studied in geological environments, however sufficient thermodynamic information is available for discussion. (Wagman, et al, 1974, Table 35; Gatehouse, 1974). Four complexes from $HgCl^+$ to $HgCl_4^=$ exist. However because H_2S is present in most mercury deposit fluids (and is it cinnabar that is deposited), it can readily be shown that the chloride complexes are not able to carry any significant quantity of mercury (Krauskopf, 1951; Schmitt, 1962; Garrels and Christ, 1965). Extremely low total sulphide concentrations, ca. $\leqslant 10^{-25}$M, would be required in the slightly acid springs, and even less in the more alkaline waters. This rules out nearly all hydrothermal emanations, which usually have at least just detectable H_2S ($>> 10^{-25}$M).

Virtually the whole of the above discussion points to the transport of mercury as the element as being the most probable mechanism/mode. However few authors have treated it seriously or favour it; most conceed that it is possible but further state that it is very unlikely, or could only occur in very special circumstances (e.g. Krauskopf, 1951 and 1956 and Hem, 1970). Dickson and Tunell (1968) believe that it is impossible because 'some unknown oxidizing substance' is required. Dickson still held the view in 1976. The element is known to be present in hot springs by the above authors and many others (e.g. Aidin'yan and Ozerova, 1966; White, 1967; Davey and van Moort, 1974). Most persons have attributed the presence of the element to thermal decomposition of the deposited cinnabar in the presence of moving gas. If this is so at the relatively low surface temperatures ($< 100°C$), then at the higher temperatures below one must expect more cinnabar and solute dissociation. Hence it should be considered that the hypothesised solutions transporting mercury complexes could have more mercury present as the element in solution or the accompanying gas!

In 1974 Davey showed that the elemental vapour was the only major form of mercury transported in a system actively depositing cinnabar.

The transport of the element as an aqueous species is also quite feasible where the gas to water ratio is very low in the total fluid. Mercury is more than adequately soluble in distilled water: at 20°, 50° and 120°C the solubility is 0.05 ppm, 0.1 ppm and 0.95 ppm (Glew and Hames, 1971), and the solubility may be greater in natural waters (D'allaglio, 1968; Table (A.11). (The presence of oxygen and Cl^- (this work) enhance the solubility appreciably and Cl^- is probably present in all spring waters).

As discussed previously Hg^o is stable under nearly all geothermal conditions, and is therefore the most probable species mobilized and transported.

c. Deposition

Once the mercury has been transported to the deposition site, cinnabar must be produced or precipitated. This may occur by a variety of processes, which depend on the species of mercury transported, the environment and the environmental changes. It is the change in environment which causes the deposition from an otherwise stable fluid. The main possible changes are:-

1. Temperature
2. Pressure
3. pH
4. Mixing
5. Degassing

Some of the above may in turn be caused by several factors. Temperature fall is the usual mode of temperature change; and may be caused by fluids moving through a geothermal gradient, boiling, degassing, mixing or escaping to the surface. Pressure changes are usually decreases, and may be caused by decrease in load (e.g. lithostatic to hydrostatic) as the fluid rises, degassing, condensation or escape to the surface. pH changes may occur due to oxidation (e.g. H_2S to H_2SO_4), rock/mineral buffering and reactions, mixing, degassing of volatile buffer species, boiling or precipitation. Mixing may be due to contact with other gas or liquid phases and result in concentration changes and reactions possibly followed by other changes (eg. temperature, dissolution). Degassing is usually caused by boiling or reduced pressure near the surface.

By considering the above changes able to cause deposition, feasible modes of cinnabar deposition mechanisms can be suggested. Very little direct experimental work has been done on cinnabar deposition in nature, consequently unconfirmed transport mechanisms require some thought on what happens when changes occur to the fluids involved.

Unconfirmed Mechanisms.

1. The Alkaline Sulphide Complexes.

Cinnabar (or metacinnabar) might be directly precipitated by:-

a. Temperature decrease,
b. pH decrease or
c. Total sulphide decrease.

(Changes in pressure have little influence on the solubilities (Dickson, 1964). The effect of dilution is not accurately predictable; but sufficient dilution can cause pH to move toward 7 once buffering is overcome. pH changes are discussed below, and dilution is apt to cause a much less efficient precipitation at best).

a. Near 100°C the complexes have a solubility minimum (Dickson, 1964) hence cooling solutions from above ca. 100 - 150°C causes cinnabar precipitation. A saturated solution cooled from the extrapolated 300°C solubility (assuming no decomposition) to ca. 100°C precipitates 30% of its mercury (Barnes and Czamanske, 1967).

b. pH decreases may cause deposition from saturated solutions of up to 90% of the dissolved mercury where pH changes from 9 to less than 5 units. For a change from a pH of 8 to less than 5 units up to 75% of the mercury may deposit (calculated from data in Barnes, Romberger and Stemprok, 1967).

c. The reduction of total dissolved sulphide concentration by an order of magnitude may cause up to about 99% of the dissolved mercury complexes to precipitate (calculated from data in Barnes, Romberger and Stemprok, 1967).

The low solubility of the complexes in usual geothermal fluids infers that deposition by temperature decrease alone is not very efficient, particularly since no decomposition is known to take place above 200°C (Dreyer, 1940; White, 1967); i.e. less than 10% of the mercury would be deposited. A change in pH is inappropriate except for alkaline springs of $pH \geq 9$. Most prospective fluids have $pH \leq 8$. For springs of $pH \leq 6.5$ probably no deposition would occur. It appears that for most springs, that only the processes which cause the total reduced-sulphide species to decrease may cause reasonable deposition of the mercury from solution (e.g. dilution, oxidation of sulphur and precipitation of other sulphides). In general if the fluids are not close to saturated with the mercury complexes the deposition processes will be rendered much less effective, except possibly in case c.

2. Chloride Species.

Mercuric chloride and the chloro-complexes are very soluble in water in the absence of H_2S (Krauskopf, 1951; Parks, 1971), hence cinnabar could be easily produced by the mixing of H_2S (aqueous or vapour) with a solution containing sufficient mercury and $pH<9$. (Mixed sulphur-chlorine species are very rare occurrences. As mentioned earlier gas carrying mercury and chlorine may directly sublime to form mercuric chloride or calomel (Hg_2Cl_2). The presence of moisture (and possibly CO_2) favour terlinguaite (Hg_4OCl_2) eglestonite (Hg_2OCl), or if ammonia is present possibly kleinite ($?Hg_2NH_2(Cl,SO_4)H_2O$) or mosesite ($Hg_6(NH_3)_2\ Cl_2(SO_4)(OH)_4$?), in

hypogene environments (Yates and Thompson, 1959). The last six mentioned chloro-compounds, probably can only form in the total absence of sulphide spcies, although sulphate may be abundant. However, none of the above-mentioned chloride minerals nor corderoite ($Hg_3S_2Cl_2$) are common mercury minerals).

d. Confirmed/Observed Mechanisms.

1. The direct combination of mercury and sulphur vapours to yield cinnabar has been reported by White and Roberson (1962) and White, Hinkle and Barnes (1970). The cinnabar is formed in very small quantities as thin coatings on fumarole mouths (White, 1976) and is called 'gas cinnabar' (ibid.).

2. a. Oxidation of mercury in acid conditions.
   b. Oxidation of mercury in neutral and slightly alkaline conditions.

In both cases the reaction proceeds only in the presence of oxygen via the equation $O_2 + 4H^+ + 2Hg^o \rightleftharpoons 2H_2O + 2Hg^{2+}$ (Davey, 1974).

In non-acid conditions Cl^- is apparently required to promote the reaction: in slightly alkaline solutions without chloride the reaction is very slow to non-existent. The mercury (Hg^o) may be present as an aqueous or adsorbed species. At Ngawha Springs the following reaction sites have been observed:

a. i. In streams and pools.
   ii. On organic materials (wood, charcoal and tars).
   iii. On marcasite.
   iv. In sediments (wet at shallow depths, interstitial).

b. v. Pools (> 25° C).
   vi. In sediments (warm, wet, deeper than a. iv., centred on fumaroles).
   vii. In marcasite.

In all seven cases once the 'Hg^{2+}' has formed, rapid precipitation with the percolating H_2S usually occurs. The reactions are only possible in open systems; i.e. a non-equilibrium situation where oxidizing and reducing conditions meet and mix. Air and surface waters supply the oxygen, and where it is relatively low in concentration, the presence of chloride increases the kinetic rates and the stability field of 'Hg^{2+}', as it does for neutral to slightly alkaline pH's. (This infers a chloro-mercury species as an intermediate in the oxidation).

Essentially i - iv require the presence of O_2, $[H^+] >> [OH^-]$ and H_2S, whereas v and vii require O_2, Cl^-, $10[H^+] \geqslant [OH^-]$ and H_2S.

The field situations in which cinnabar deposits are described later in this thesis and in Davey and van Moort, 1974 and Davey, 1974 and 1977 . Areas producing the most cinnabar fall into category vi.

3. Cinnabar via bacterial action.

Aqueous oxidized mercury (formed per the above section) in some environments which are low in sulphide and high in sulphate may form cinnabar (Davey, 1977). At the water-sediment interface in streams, biotic reduction of sulphate on organic matter causes aqueous mercury II to combine with the sulphide produced. The resulting cinnabar and other sulphides pseudomorph the organic material (Figure (6.3)). The process is described in detail later.

4. Condensation of Mercury.

Many of the gases at Ngawha Springs are saturated with mercury and hence deposit liquid mercury, much of which diffuses into the surrounding ground, the atmosphere and various waters. During the movement of the mercury, some of it also becomes fixed as cinnabar (and possibly other minerals) by mechanisms as described in part 2 via oxidation. Due to the (wide) dispersal of the mercury it is uncommon to detect cinnabar formation, however some was noticed to form on a film of mercury metal not far from a small, hot fumarole (ca. 45°). Some cinnabar dustings on charcoal form by a similar mechanism, and probably constitute the most widely dispersed cinnabar forming in the field which is visible to an unaided eye.

CHAPTER THREE GEOLOGY

(3.1) REGIONAL GEOLOGY OF NORTHLAND

Northland is formed from dominantly sedimentary rocks belonging to three successive sedimentary associations each of which is accompanied by characteristic igneous rocks (Leitch, 1975). A major break in the deposition occurs about 90 M.Y.B.P. between pre-Late Cretaceous rocks and younger strata. Deformation accompanied the break; the next change in sedimentary association was some 65 M.Y. later (25 M.Y.B.P.). Deposition in the youngest association ended about 15 M.Y.B.P., but no deformation related to this event has been demonstrated. The first major break is considered to be a manifestation of the Rangitata Orogeny, whilst the second is associated with the Kaikoura Orogeny.

a. Permian - Late Cretaceous

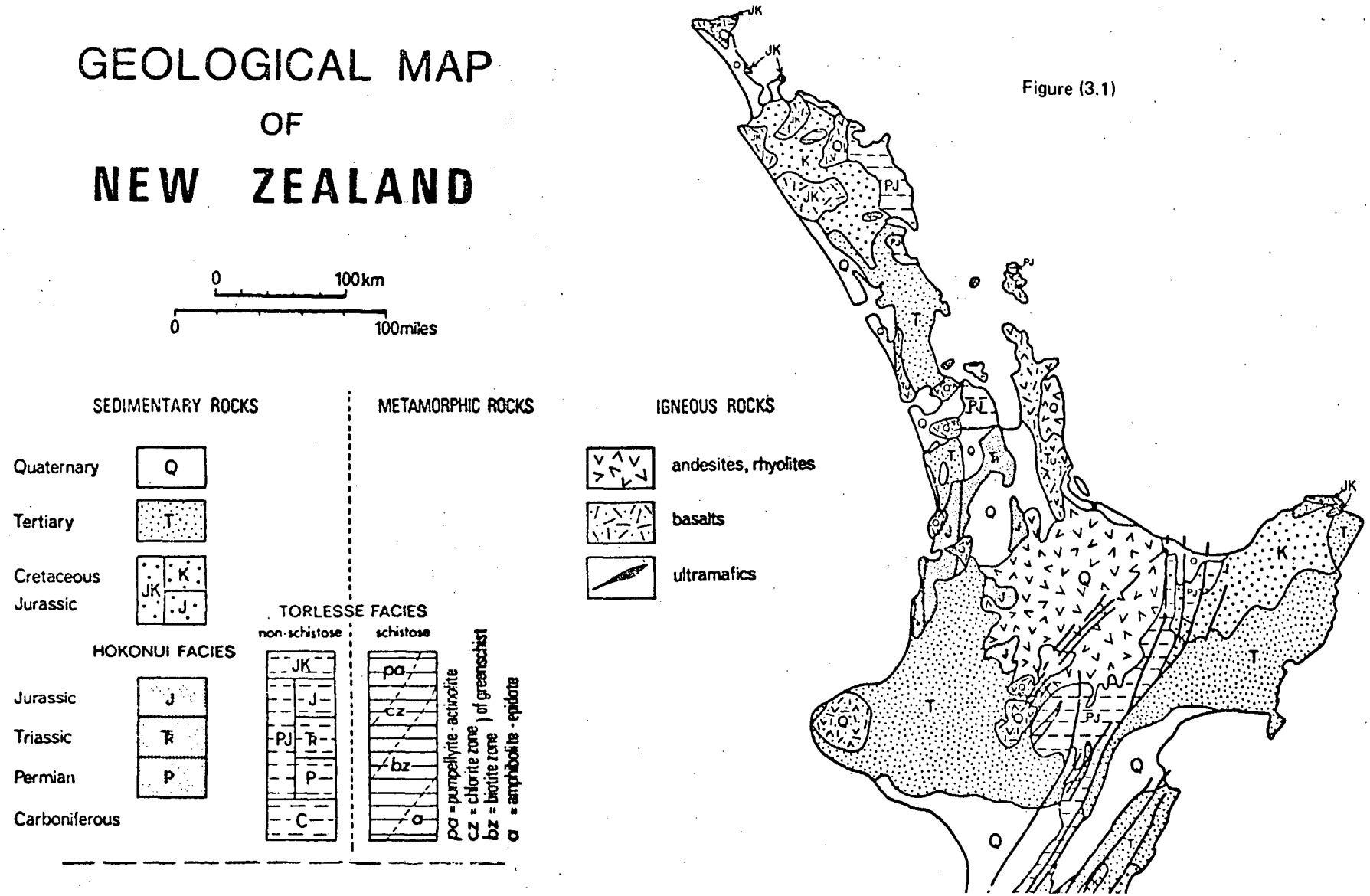
The oldest known rocks belong to the Waipapa Group which outcrops in the east, where it contains fossils of Permian to Jurassic age (Torlese Facies) in the coastal exposures (Figure (3.1)). The group forms the basement and consists of greywackes and argillites with intercalations of marine basalts, and lenses of limestone, chert, and quartzite (Kear and Hay, 1961; Skinner, 1966; Leitch, 1975). The basement has been weakly metamorphosed on a regional scale to prehnite-pumpellyite or pumpellyite-actinolite grade (Brothers, 1974).

The structure is not well known, but generally the basement dips south-west with major faults of north-north-west to north-west strike and a younger set, which strike east-north-east to north-east. Folding is absent to very slight in the central and western-most exposures and it becomes a little more obvious in the extreme eastern exposures where the axial trend is north-north-west. This contrasts the oldest rocks of the younger western exposures where the structure is far more complex.

About the end of the Jurassic the Tangihua Volcanics began to form in a trench to the east of the Permo-Jurassic basement (Griffiths, 1973; Brothers, 1974) and a major unconformity (ca. 90 M.Y.) developed which separates Upper Cretaceous to Recent rocks from the peneplaned basement.

b. Late Cretaceous - Late Oligocene

Between about 90 and 25 M.Y.B.P. the depositional history and structure are poorly understood. A large variety of sediments were laid down, and all the older rocks of the interval are thought to be allochthonous (Kear and Waterhouse, 1967; Griffiths, 1973; Brothers, 1974; Leitch, 1975).


GEOLOGICAL MAP
OF
NEW ZEALAND
0
100km
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SEDIMENTARY ROCKS
METAMORPHIC ROCKS
IGNEOUS ROCKS
Quaternary
Q
Tertiary
T
Cretaceous
Jurassic
JK
K
J
andesites, rhyolites
basalts
ultramafics
TORLESSE FACIES
non-schistose
schistose
HOKONUI FACIES
Jurassic
Triassic
Permian
Carboniferous
J
Tr
P
C
PJ
pa
cz
bz
a
pa = pumpellyite - actinolite
cz = chlorite zone
bz = biotite zone
a = amphibolite - epidote
of greenschist

Figure (3.1)

The sediments are mudstones, sandstones, a variety of coloured shales, limestones, siltstones, concretionary micaceous sandstone with carbonaceous material, coal and glauconitic sandstone (Kear and Hay, 1961). These are less indurated than pre-Late Cretaceous rocks, and typically lack contemporaneous lavas or igneous lithic fragments. The total stratigraphic thickness is of the order of 7,000 m (Brothers, 1974)

The sandstones are notably micaceous, and conglomerates contain argillite, minor granite and altered igneous rock (Leitch, 1975). However, no source is exposed or known in Northland to account for the mica and the granite (nor the basic Tangihua Volcanics which are rootless).

As yet there is little agreement on the extent of allochthonous material, nor the time, the duration and the direction of its emplacement. Kear and Waterhouse (1967) state that " . . . there is no certain proof that any of the Upper Cretaceous - Paleocene rocks are autochthonous anywhere in Northland, and that a major effort is required to confirm that all areas of these rocks are not part of the Onerahi Chaos Breccia." The chaos breccia seems to have formed between the uppermost Oligocene and the Pliocene.

c. Miocene, 23 - 15 M.Y.B.P.

Coinciding with the commencement of Miocene volcanism throughout Northland was the subsidence of depositional basins (Ballance, 1974; Leitch, 1975). The basins filled with conglomerate, sandstone and siltstone intercalated with volcanic flows, pillow lavas and pyroclastics. Igneous material was a major sediment source along with detritus from older rocks, especially the basement greywacke.

d. The Chaos Breccia.

(The bulk of the text has been adapted from Kear and Waterhouse, 1967).

The breccia has been shown to be an olistostrome. It is a near surface incompetent sheared, chaotic breccia of Upper Cretaceous to Miocene rocks, and locally Pliocene sediments. It has typical slump topography; a subdued hummocky surface with few outcrops. It occurs scattered throughout Northland over limited areas below 35° south, and has a proven probable distribution totalling more than 25 km^3, although it rarely exceeds 350 m thickness. Because of the usual deep weathering, mismapping of the formation has been common, and hence the extent of the breccia may be much greater than that currently known.

The chaos consists of sheared angular fragments ranging from clays to boulders which weigh over 50,000 tonnes. The matrix is usually sheared mudstone. However

near Ngawha the outcrop is an intensely sheared and highly calcareous argillitic shale. Most notable is the lack of discernable bedding in outcrops, drill-cores and fragments.

The formation commonly has sharp unweathered contacts with facies in the range Permian-Jurassic to near basal Pliocene, and partly overlies one Quaternary basalt flow near Ngawha. The surface of the underlying rock is normally highly eroded but contacts are fresh, and hence are likely to be relatively recent. The breccia appears to fill fossil valleys that occur near low-lying valleys of recent time, where it is usually overlain by Quaternary basalt or alluvium. Hence the chaos was probably most widespread in the Pliocene when it would have been on the surface in Northland. The chaos breccia also occurs in areas along the apparent major contact between the eastern Waipapa Group facies (Torlese) and the Upper Cretaceous-Lower Eocene rocks in western and central Northland.

It is generally conceded that the mechanism of formation of the Onerahi Chaos Breccia was gravity sliding caused by block faulting, although there is always a conspicuous absence of adjacent elevated ground. The formation totally lacks bedding and so was probably formed by a long series of movements.

Emplacement of the allochthonous material probably took place between the Oligocene-Miocene and the Quaternary, and was associated with the Kaikoura Movements (Ballance, 1974; Leitch, 1975). During the early part of this interval major block faulting probably initiated the chaos breccia. There is still considerable conjecture about the source(s), time, duration, overall mechanism and the direction of emplacement, as well as the extent of the breccia. Kear and Waterhouse (1967) favour emplacement from the west; however others favour an eastern source (Brothers, 1972; Griffiths 1973; Leitch, 1975; Ballance, 1976). It is also concluded that the Tangihua Volcanics similarly came from the east by being underthrust. Brothers (1974) states that their emplacement coincided with the tectonic climax in the uppermost Oligocene when there was east to west gravity sliding of an internally disrupted plate of Upper Jurassic oceanic igneous rock (Tangihuas) and Cretaceous-Oligocene sedimentary formations.

e. Igneous Rocks.

Northland is dominated by an arcuate band of basaltic rocks ranging in age from Jurassic to present day. Flanking these rocks are other extrusive igneous rocks also distributed as westward concave arcs according to type (Thompson, 1965). The arcuate distribution continues further south as the rocks young, and eastwards as they become more acid. The pattern is less obvious in Northland than in the southern continuations of the volcanic arcs which currently reach Mt. Ruapehu (Quaternary andesite). Anomalies in zonation occur, but are small compared with the overall distribution in the North Island of New Zealand.

The main pre-Late Cretaceous igneous rocks are the North Cape Ultramafics, the basic marine lavas in Waipapa Group (basement) and probably the basic Tangihua Volcanics (Kear and Hay, 1961; Thompson, 1965; Brothers, 1974). North of 35° S the Jurassic - Early Cretaceous basalt and rhyolite contain intercalated sediments which are probably associated with a gabbro-peridotite mass, the Kerr Pluton at North Cape (Leitch, 1975), which resembles many ophiolite complexes. Plutonic rocks occur mainly to the east of the Northland axis and northwards from Whangaroa Harbour.

The Tangihua Volcanics extend south-south-east for about 175 kilometres along the axis of Northland to Wellsford (Brothers, 1974). In the central north they outcrop 300 m above the surrounding country of soft Cretaceo - Tertiary sediments, which lie south-west of the Mesozoic greywacke blocks. The volcanics are of basic marine type with flow and pillow lavas and lack roots. They are commonly interdigitated with sediments, especially of Cretaceous - Oligocene age. The contacts are highly sheared and brecciated, and the adjacent sediments are poor in volcanic detritus; consequently the volcanics are believed to be allochthonous. Each massif is also fault-bounded against Cretaceous - Oligocene sediments. The age of the volcanics is uncertain, but they are interdigitated with a wide range of sediments where fossil ages range from Upper Jurassic to Lower Miocene (Brothers, 1974). The older age (Tithonian) is favoured. The rocks are said to be tholeiitic, but they are unusually enriched in alkalies (Brothers, 1974).

The igneous rocks of the Tertiary and Quaternary are better preserved and consequently somewhat better 'understood' (Stipp and Thompson, 1971; Brothers, 1974; Leitch, 1975; Ballance, 1976). Widespread are basaltic rocks of several types, including the Waipoua (Miocene), Horeke (Pleistocene), Auckland (Quaternary) and Taheke (Holocene) Basalts, which stretch over 350 kms south from Whangaroa Harbour. They are most extensive in the area between the Hokianga, Whangaroa and Whangarei Harbours: this includes the Kaikohe Volcanic Field. The basalts occur as flows forming extensive plateaux (Waipoua Basalt), terraces or small plateaux up to 200 m A.S.L. (Horeke Basalt) to cones and flows on valley floors (Taheke, Horeke Basalts).

The basalts are all post late Oligocene and probably less than ca. 23 M.Y.B.P. The oldest dated basalt (K/Ar) is 15.1 M.Y. (Stipp and Thompson, 1971) and is not the earliest volcanism (Ballance, 1976). The first phase of volcanism is regarded as Waitakian/Otaian in age, ca. Early Miocene, and commenced along the present west coast and shelf and slowly moved east, extruding mixed lava types: andesite, andesite-basalt and basalt. (The fossil age range of the Tangihua basalts overlaps the Lower

Miocene, however the volcanics are probably allochthonous and have incorporated the youngest fossil bearing sediments long after extrusion, during tectonically induced movement(s)).

Ultrabasic rocks occur in small scattered bodies between Wellsford and Silverdale (Thompson, 1965). The ultramafics are serpentenised rootless masses associated with the Onerahi Chaos Breccia of possibly Miocene or Pliocene age (Skinner, 1966). One ultramafic body has been dated at 11.9 M.Y.B.P. by Stipp and Thompson (1971).

Andesites of about lowermost Miocene to late-Pliocene occur in two major bands of intermittent occurrences in Northland; these run south close to the east and west coasts. The eastern zone starts at Whangaroa, leaves Northland near Mangawhai and extends south-east then southwards to Mt. Ruapehu. The western band terminates at Mt. Egmont. (Both mountains are large Quaternary volcanoes which are probably still active).

The northern portion of the western volcanic belt consists of andesitic basaltic lavas and breccias which are mostly out to sea. The eastern zone contains breccias, minor lavas and plugs which are grouped as the Wairakau Andesites in Northland which date as young as 4.3 M.Y. in the north, near Whangaroa Harbour, and as old as 15.7 M.Y. at Bream Head, ca. 80 km south-east of Ngawha Springs (Stipp and Thompson, 1971).

Dacitic rocks are closely associated with Tertiary andesites, and faults in the basement greywacke (Thompson, 1965; Leitch, 1965; Ballance, 1976). They occur only in the east of Northland and out to sea except for an occurrence near Tokatoka, 45 km south-west of Whangarei. One of the earliest flows has been dated at 17.7 M.Y. B.P. at Bald Hill west of Mangawhai (Stipp and Thompson, 1971). Earlier flows are associated with the low-potash andesites flows of about 16 M.Y. to 4.3 M.Y.B.P., whereas younger dacites tend to be associated with rhyolite from about 6 M.Y.B.P. to 3 M.Y.B.P. in Northland, and to ca. 0.75 M.Y.B.P. in the area to the south-south-east of the Coromandel Peninsula.

To the north of Ngawha Springs three (?) Pliocene rhyolite domes lie in a line running north-north-east from Putahi near Kaikohe (Kear and Hay, 1961; Thompson, 1965). Two are partly surrounded by Horeke basalt flows.

Northland has few plutonic rocks of Caenozoic age. The few outcrops are small, and are either dikes or small plutons with Middle Tertiary sediments and volcanics in the east of Northland. Most occur in the area to the east of Whangarei, and include a granodiorite porphyry near Bream Head (Thompson, 1965).

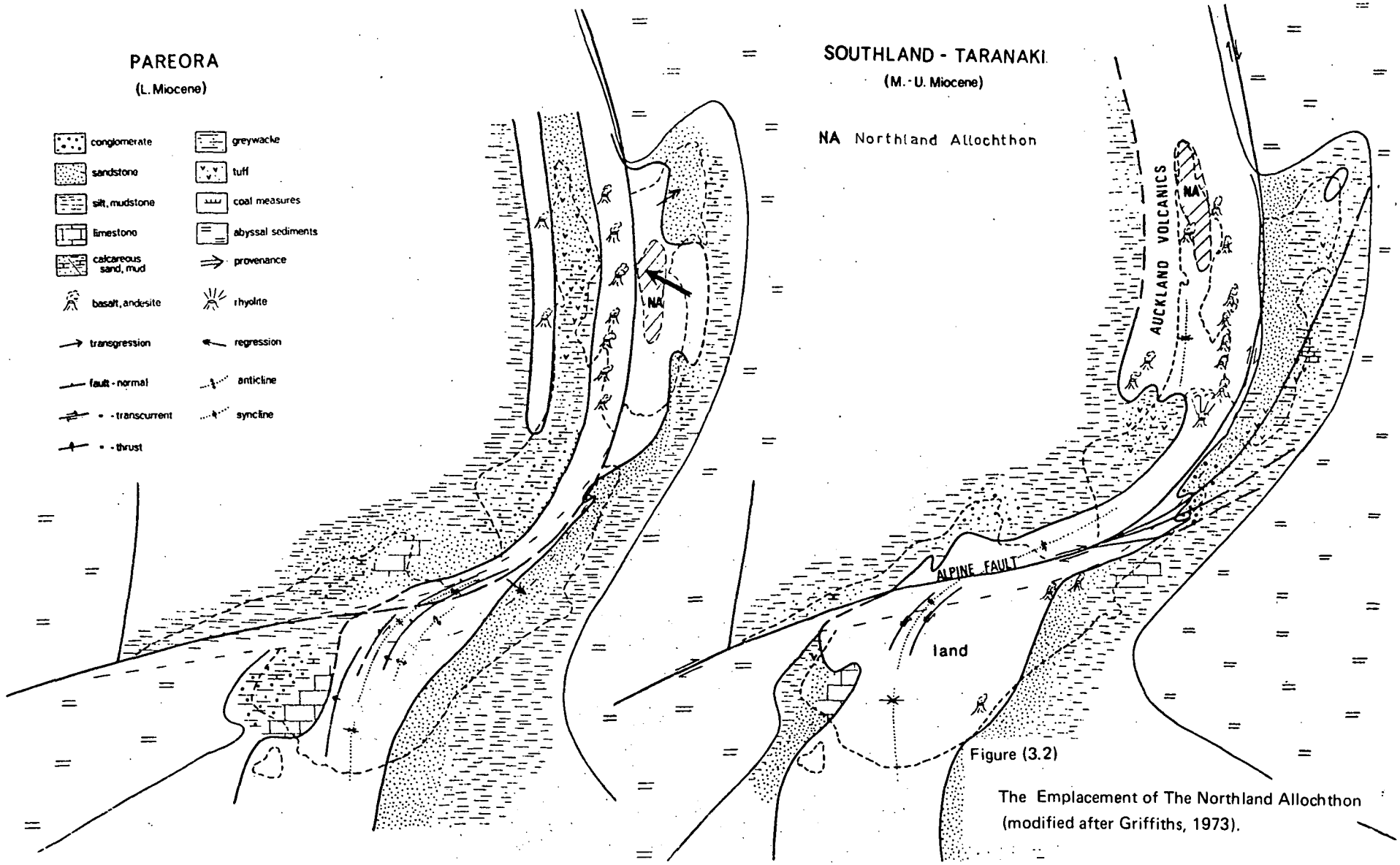


Figure (3.2)

The Emplacement of The Northland Allochthon (modified after Griffiths, 1973).

(3.2) REGIONAL HISTORY

The earliest geological record exposed in Northland is the Permian - Upper Cretaceous basement greywacke which is akin to eugeosyncinal sediments deposited on a continental slope adjacent oceanic crust (Leitch, 1975). There is an equivalent shallow-water facies (Hokonui) exposed less commonly in the west (Figure (3.1)). The western facies was deposited on probable marginal continental crust and the exposures tend to be younger than in the east. Griffiths (1973) matches these facies with very similar ones further south, where a landmass to the west existed during the time of sedimentation. The presence and nature of volcanic remnants in the sediments have led Griffiths (1973) and Leitch (1975) to conclude that a subduction zone dipped west beneath the sediments, (the New Zealand Geosyncline), from the Early Permian to possibly the Early Cretaceous.

Currently the basement abruptly disappears under a syncline of sediments to the west which contains the basaltic Tangihua Volcanics, the Mt. Camel Volcanics and the North Cape Ultramafics (Wellman, 1956; Griffiths, 1973; Leitch, 1975). The volcanics are in the same age interval as the basement with which there is no direct association. Consequently it is believed that this group of volcanics and associated sediments were emplaced 'en mass' about the Middle or Upper Miocene. The mechanism is not well understood, however it is generally thought that a huge mass, the 'Northland Allochthon' (Griffiths, 1973; Brothers; 1974) came from the east (Figure (3.2)). (There are striking similarities between the lithologies of the allochthon and those of the same age in the north-east and eastern portion of the North Island of New Zealand)

Deformation and metamorphism up to pumpellyite-actinolite facies (Brothers, 1974) occurred at the end of the Early Cretaceous and is attributed to the failure of subduction: Leitch (1975) suggested that there was temporary coupling of the Australia and Pacific plates. This is known as the Rangitata Orogeny. It had started much earlier further south, ca. Middle Jurassic, and caused more intense effects. The orogeny uplifted Northland, particularly the east, and continued until the Upper Cretaceous. Between these epochs most of Northland was subaerial, and by the end of this time the Tangihua Volcanics had formed in the east.

Brothers (1974) suggested that the environment of formation of the Late Cretaceous - Early Tertiary rocks was a trench related to eastward dipping subduction. The subduction zone was to the east and deformation at the end of the period (ca. Upper Oligocene) resulted from blocking of subduction by the sialic mass of Northland: the Kaikoura Movements (or Orogeny). Griffiths (1973) also suggested a lack of subduction. Tilting of Northland, after reversal of subduction polarity (to west) then

caused a westward gravity flow of allochthonous material, including the Tangihua Volcanics (Upper Jurassic oceanic crust) (Griffiths, 1973). Other authors believe the material, or some of it, came from the west (Wellman, 1956; Kear and Waterhouse, 1967).

There is a notable lack of high pressure metamorphism and deformation which would be expected from a continent-arc collision (Leitch, 1975). He favours the period 90 - 25 M.Y.B.P. as a time of active rifting associated with the opening of the Tasman Sea: incipient rifting of Northland induced a marine transgression accompanied by effusive basic volcanism in the Upper Cretaceous (the Tangihua Volcanics) in an area of low relief. The main problem with this idea is the interdigitation of the volcanics with much later sediments; volcanics do not appear in situ and have extremely sheared contacts, and notably stand above the younger surrounds. Leitch suggests that his interpretation better explains the alkaline nature of the rocks and the total lack of high pressure metamorphism.

Marine transgression began in the Upper Paleocene and nearly all Northland was submerged during the Oligocene to Middle Miocene (Griffiths, 1973; Leitch, 1975)

Tectonic activity began in the Upper Landon Series (Lower Middle Oligocene) and land area increased. This was the Kaikoura Movements or Orogeny which manifested itself locally as gentle folds (Brothers, 1974; Leitch, 1975). In the Lower Miocene marine regression continued and volcanic activity broke out along the west coast (Ballance, 1976). Shortly after this the Northland Allochthon was finally emplaced (?) ca. Early to Middle Miocene, and Northland had become mostly subaerial (Griffiths, 1973).

The early Miocene to the present is by contrast well understood due to the relatively fresh state of the rocks, their dominantly autochthonous nature and radiometric dating. From about 23 M.Y.B.P. to the present there has been a tectonic plate boundary present in New Zealand (Griffiths, 1973; Ballance, 1975) and six associated volcanic arcs (Ballance, 1976). Only the first four arcs have been present in Northland, but behind the arc activity took place with the last two as the arcs have progressed eastwards then south-eastwards relative to the Northland peninsula. There has been a gradual increase in acid volcanism from almost exclusively calc-alkaline volcanism, and with the progression of the arcs there has been an associated steepening of the Benioff Zone from ca. 18° to a current 60° (Ballance, 1975). During the last three million years Northland has been rotated anticlockwise by 70 - 75° with respect to the rest of the North Island (Ballance, 1975; Wellman, 1975). During the last 20 M.Y. there has also been a 230 km dextral transcurrent movement of the western part of the island against the east.

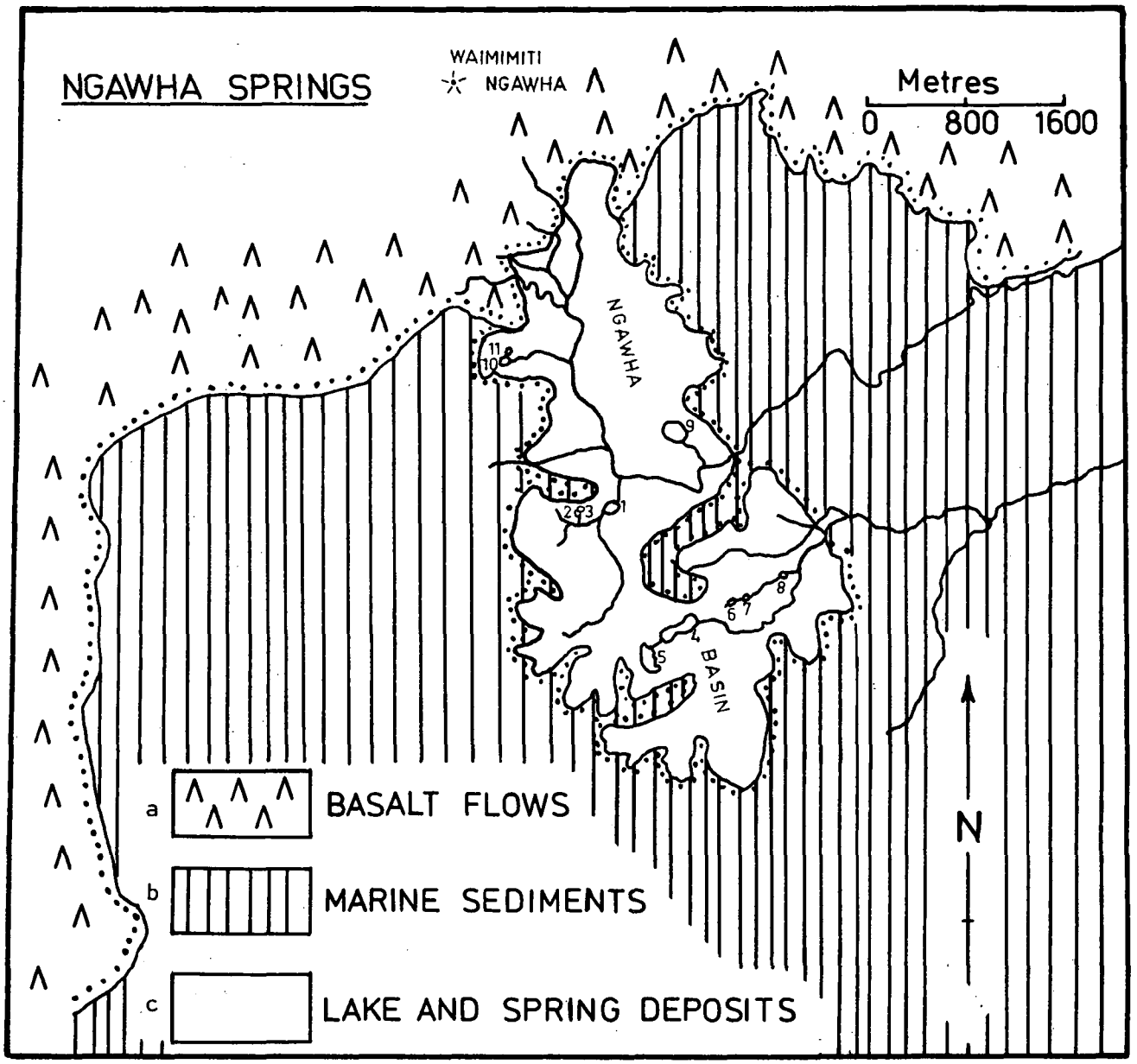
The first arc was present along the west coast from just prior to 20 M.Y. (Stipp and Thompson, 1971; Leitch, 1975 and Ballance, 1976). The lava types were mixed, and were mainly andesite, andesitic basalt and basalt with rare dacite (Thompson, 1965 and Ballance, 1976) and issued until 15 M.Y.B.P. Partly contemporaneous with the first arc, a second became active from 18 to 15 M.Y.B.P. almost 100 km further east. Far more of the volcanism was subaerial than that in the west; the lavas were dominated by calc-alkaline andesite and dactite with minor rhyodacite and basic forms. Flysch bodies (e.g. Waitemata Group) formed in the irregularly subsiding inter-arc body (Ballance, 1976).

Between 16 and 6 M.Y.B.P. andesite and dacite volcanism from a third parallel arc displaced slightly further east occurred. At the beginning (ca. 15 M.Y.B.P.) substantial block faulting took place (Ballance, 1976) and is probably responsible for at least part of the Onerahi Chaos Breccia. In modern Northland the volcanics are present only in the extreme east (Bream Head), and the northern end of the volcanics has been eroded away (Ballance, 1976). During the interval two occurrences of undersaturated basic volcanics also appeared and they have been dated (Stipp and Thompson 1971). Associated with a fourth arc considerably overlapping the former, large quantities of rhyolite and ignimbrites appeared, however in Northland there was only minor rhyolite. Mostly andesitic volcanism occurred, e.g. the Wairakau Andesite Breccia, 4.3 M.Y.B.P. The fourth phase of arc volcanism ended about 3 M.Y.B.P., and was separated from the third by an interval of erosion.

Since 3 M.Y.B.P. significant flows of high alumina to alkaline basalts had occurred in three fields by 0.75 M.Y.B.P. (Ballance, 1976). In particular the Horeke Basalts in the Kaikohe volcanic field exuded between 2.7 and 0.5 M.Y.B.P. (Mulheim, 1973). From ca. 0.02 M.Y.B.P. another series of basalt flows, the Taheke Basalts, have appeared in the Ohaeawai area. Also in the Ohaeawai - Whangaroa area, three small rhyolite domes have formed since ca. 0.75 M.Y.B.P. (Kear and Hay, 1961; Thompson, 1965 and Ballance, 1976), and during that time interval Northland rotated 30° into its present position.

It has only been during the last six million years that mineralisation has been associated with the volcanism, apart from a few minor occurrences (Ballance, 1976).

Figure (3.3) The Geology of The Ngawha Region



Geology of the Ngawha Region:

a - Horeke and Taheke basalt flows
b - Includes the Northland Chaos Breccia
c - The cover is dominantly lake sediments.

1 = Tuwhakino Pond; 2 = Sulphur Pool; 3 = Soda Pool; 4 = Waiparaheke Pond; 5 = Ngamokaikai Pond; 6 = Upper Sulphur Pond; 7 = Middle Sulphur Pond; 8 = Lower Sulphur Pond; 9 = Waiapawa Pond; 10 = Waitotera Pond; 11 = Little Waitotera Pond.

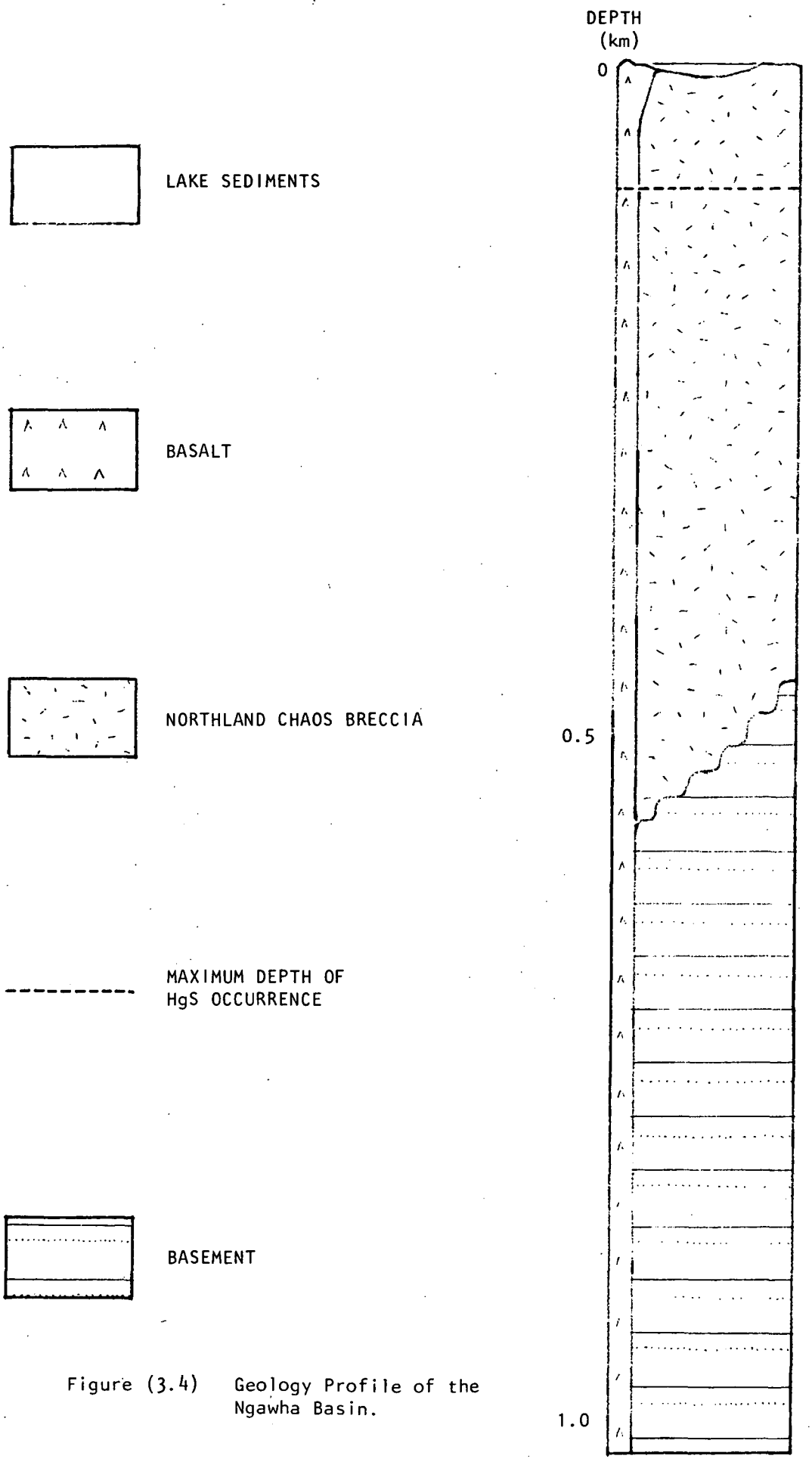


Figure (3.4) Geology Profile of the Ngawha Basin.

(3.3) LOCAL GEOLOGY

(The local geological environment consists of rocks, soils and hydrothermal associations).

The Ngawha springs lie in a basin formed in Upper Cretaceous marine sediments and an olistostrome of Upper Cretaceous to ca. Miocene marine sediments (Skinner, 1966 and Figure (3.3)). The basin occupies 15 km^2, and has a superficial veneer of lacustrine sediments up to 14 m deep covering 11 km^2. The dominant facies of the area is the chaos breccia (olistostrome) which underlies most of the basin and beyond to an unknown extent. The breccia is 600 to ca. 215 m thick and probably overlies the basement greywacke (Thompson and Kermode, 1965; Skinner, 1966). Quaternary basalt flows outcrop in most directions except the south-east. The basalt overlays the chaos breccia (with one exception) and the Upper Cretaceous shallow-marine shales and sandstones, and underlays the lacustrine sediments (Figure (3.4)). Within the greater basin area there is anomalous heat flow (Banwell, 1965), however all surface expressions of recent and current geothermal activity are confined to the area covered by the lake sediments and not underlain by basalt.

a. The Basement

The basement Waipapa Group gently dips south-west at 1 - 5° from its surface exposures 15 km to the east and north-east of Ngawha Springs, and is broken by two sets of major faults: ca. mid-Cretaceous to ca. early Paleocene of north-north-west strike and late Tertiary of east-north-east strike (Kear, 1961 and 1964; Kear and Thompson, 1964; Brothers, 1965 and Leitch, 1975). There are no outcrops close to the basin and drilling shows that the basement is unlikely to be shallower than ca. 500 m (Bowen, 1966).

b. Tertiary Rocks

The local chaos breccia, now called the Northland Chaos Breccia (Skinner, 1976) was known as the Onerahi Chaos Breccia until recently. It probably lies directly on the basement. The formation contains microfossils ranging from Permian to Pliocene (Hornibrook, Scott and Edwards, 1966; Kear and Waterhouse, 1967) in dominantly shallow marine sediments. The breccia has been mismapped as part of the Paleocene Mangakahia Group of shales and sandstones, possibly due to the large outcrops of brecciated shale 1.5 km east of Ngawha Springs. It is extremely difficult to estimate the extent of the breccia since no clearly discernable contacts and few outcrops exist in the field area. There are at least 6 and possibly up to ca. 25 square kilometres of the breccia in the basin and to the east-north-east along the Ngawha stream.

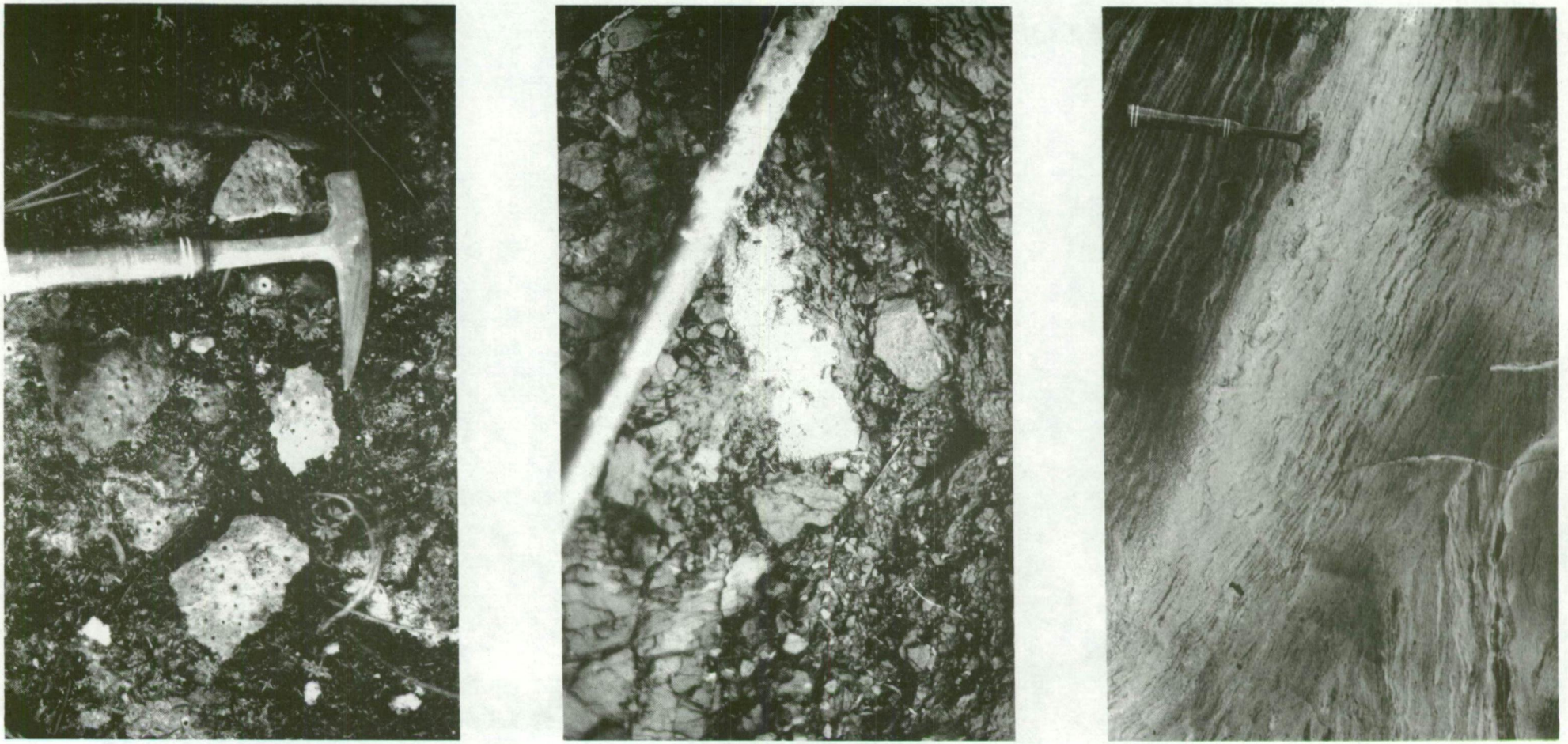


Figure (3.5) A: The Lake Sediments, 1/9x. The sediments display compositional banding and slumping textures. Compositional changes are mostly due to varying amounts of organic material. Slumping and sliding seem to have been common throughout the basin near the present streams. B: Rafts of the Lake Sediments in geothermally disturbed (pelitic) sediments: 1/3x. C: Holes caused by gas evolution common throughout the basin near zones of geothermal activity, 1/5x. Picture taken near Ngamokaikai Pond.

The chaos breccia differs from other Northland occurrences. It is the thickest known occurrence (Kear and Waterhouse, 1967) and is unusually high in altitude (185 m). It is more calcareous (in major portions), wider ranging in age, and is apparently without serpentine. The deep drill-hole NG1 showed only the presence of the breccia to 591.3 m, and progressed from mainly siltstones, shales and sandstones; sheared calcareous siltstones; argillites changing to harder calcareous siltstones and sandstones to argillites with minor sulphides and carbonaceous matter as depth increased (Skinner, 1966). At the small landslip along the Mangamutu/Ngawha stream (Figure (1.3)) the breccia contains boulders of limestone (micrudite) in a dominantly fine grained mass of calcareous grey shale with minor iron sulphides, whereas the two larger land-slips lower down-stream contain grey calcite-rich pelitic shales and subordinate argillitic shales.

The presence of the chaos breccia is accompanied by subdued topography except where streams traverse: there the water may cut deeply into the breccia. Hills of the material commonly have earth flows and large gouges on their slopes as may river channels. Consequently it is noteworthy that the hills to the north-east of Ngawha Springs (on the southern side of the Ngawha Stream) are higher than the rest of the chaos areas and 40 to 65 m higher than the water course 220 m away, i.e. a slope exceeding 1:6. The prior-mentioned land-slips lie directly between the hottest thermal zone and the youngest volcano in the area, Pouerua. Hence uplift on the south-eastern side of the Mangamutu Stream probably has occurred recently. The area between Pouerua and the springs is probably a fault zone (Figure (3.6)); slicken-siding was found at the smallest slip (N15/378350).

c. Quaternary Sediments

Overlying the major portion of the basin are lake sediments which form a low-lying and embayed area of subdued topography, labelled 'Lake and Spring Deposits' in Figure (3.3). The sediments cover ca. 11 km^2, have a maximum thickness of ca. 13.5 m. Outcrops are confined to water courses and rarely expose more than the surface 2 m. The lake deposits are derived from the local country rocks and are pale, mostly coarse, angular quartz fragments of up to 1.5 mm diameter, with a subordinate fine-grained matrix. Peat commonly occurs in the uppermost layers.

The sediments are poorly to moderately well sorted, and show fine bedding Figure (3.5). The lake deposits are unconsolidated and hence extremely friable. Erratic dips and some cross-bedding occur only in the lower levels of the sediments towards the centre of the basin (especially about the western end of the Tuwhakino Stream). Dips rarely exceed 16° and no hydrothermal minerals are present in undisturbed sediments close to thermal sites. It is thus probable that slumping occurred over steep

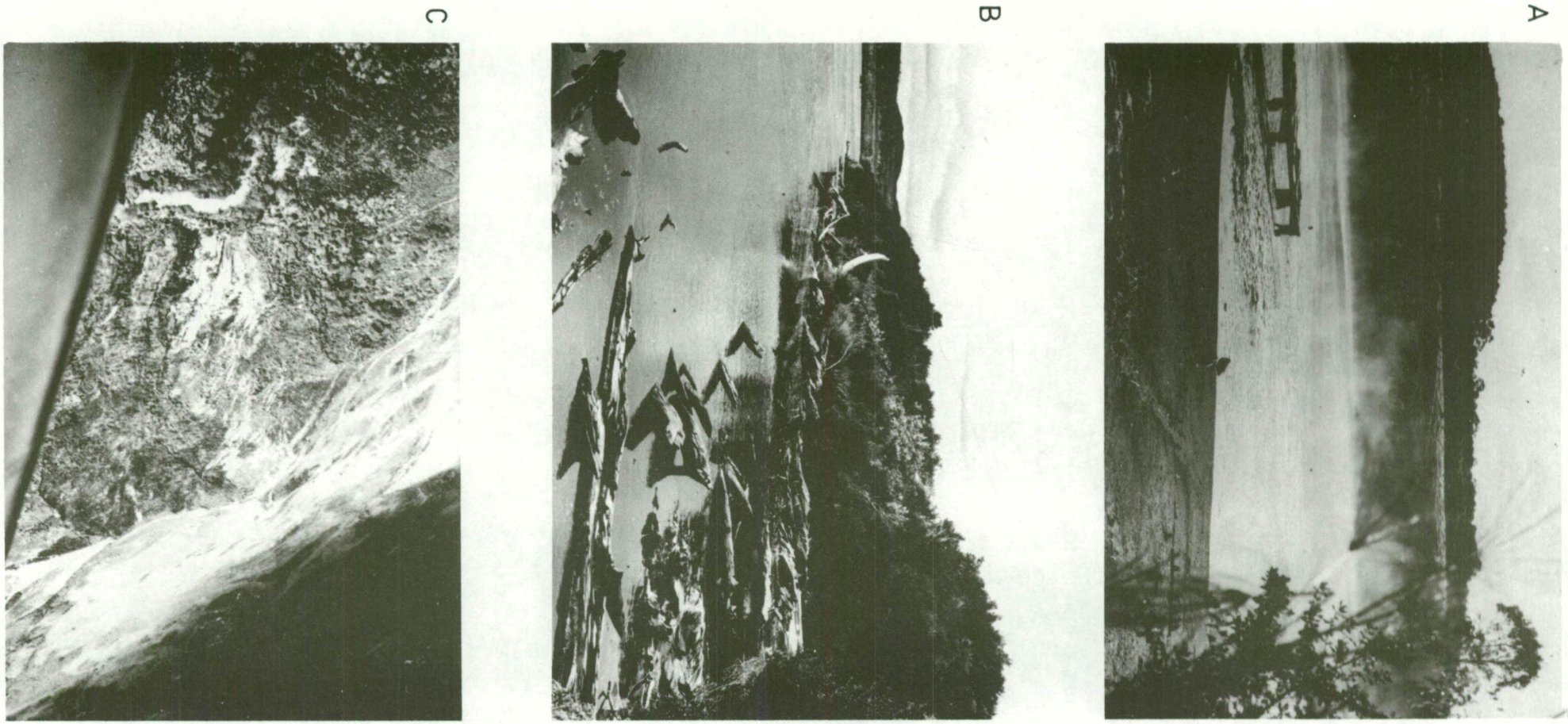


Figure (3.6) A: Tuwhakino Pond, the largest of the pools in the central thermal area, and adjacent to the hottest geothermal bath in the entire Ngawha Basin. B: Waiparaheke Pond, in the southern zone of thermal activity is the largest lake in the basin. In the foreground are the remnants of a decimated forest which fell shortly after thermal activity broke out about 6850 years ago. The ebullience of the activity sapped sediments about stream courses and caused the local forest to collapse as the land gave way. C: An aerial infra-red photograph of the area near the 'small slip' (N15/358350) by the Ngawha Stream. Lines of dextral 'shearing' show up on the photograph centre. The area lies on a line between Pouerua (the youngest volcano in the area) and the most thermally active ground in the Ngawha Basin. the land-slip has increased considerably since 1950.

parts of the lake floor. A few blocks of lake sediments have been tilted slightly where geothermal activity and/or sapping of sediments have been greatest.

d. Quaternary Igneous Rock

All igneous rocks in the Ngawha Basin and environs are young extrusives ranging from ca. Pliocene to Recent (Kear and Thompson, 1965; Brothers, 1965). The rocks in probable sequence of eruption are:

i.	Te Pua Andesite (craters and flows)	,	ca. $\leqslant$ 4 MYBP
ii.	The Horeke Basalts (flows only)	,	2.3 - 0.52 MYBP
iii.	The Putahi Rhyolite (dome)	,	ca. I MYBP and
iv.	The Taheke Basalts (scoria cones and flows	,	0.02 $\leqslant$ 0.001 MYBP

(Kear and Thompson, 1964; Stipp and Thompson, 1971 and Mulheim, 1973). The above rocks form the Kaikohe Volcanic Field of which the Ngawha Basin is part. The basin contains only flows of the two basalts, consequently only they are described below.

The Horeke and Taheke lavas form the Kerikeri Volcanics, of which there are more than twenty and ten flows respectively (from combined information in Kear and Hay, 1961; Kear, 1961; Kear and Thompson, 1964; Skinner, 1966; and Mulheim, 1973). The volume of erupted Kerikeri lavas has been estimated to be near 45 km^3 (Kear and Thompson, 1964), with each centre averaging 1 - 2 km^3 of lava. The Kaikohe Volcanic Field is at the southern end of volcanism which has steadily moved south and east. There are about nine volcanic centres within ten kilometres of Ngawha Springs; seven are the younger Taheke basalts, and include a scoria cone and flows less than 5,000 years old (Pouerua in Mulheim, 1973). The youngest flow also lies along the fault which contains the most vigorous geothermal activity at Ngawha Springs.

(3.4) A BRIEF LOCAL HISTORY

Nearly 40,000 years ago an Horeke Basalt dammed the basin, then a valley which drained northwards into the Waitangi River. (Other flows of basalt had entered the valley previously (Bell and Clarke, 1909)). A lake formed and remained until it broke out to the north-east at two places: the Mangatawai and Mangamutu streams. Erosion of the two drainage saddles caused the lake to recede entirely and eventually a forest formed. The draining was prior to ca. 25,000 YBP when already a kauri forest had begun to replace peaty swamp. Some areas have remained swamp until very recently.

Geothermal activity broke out about 6,900 YBP. The thermal activity and

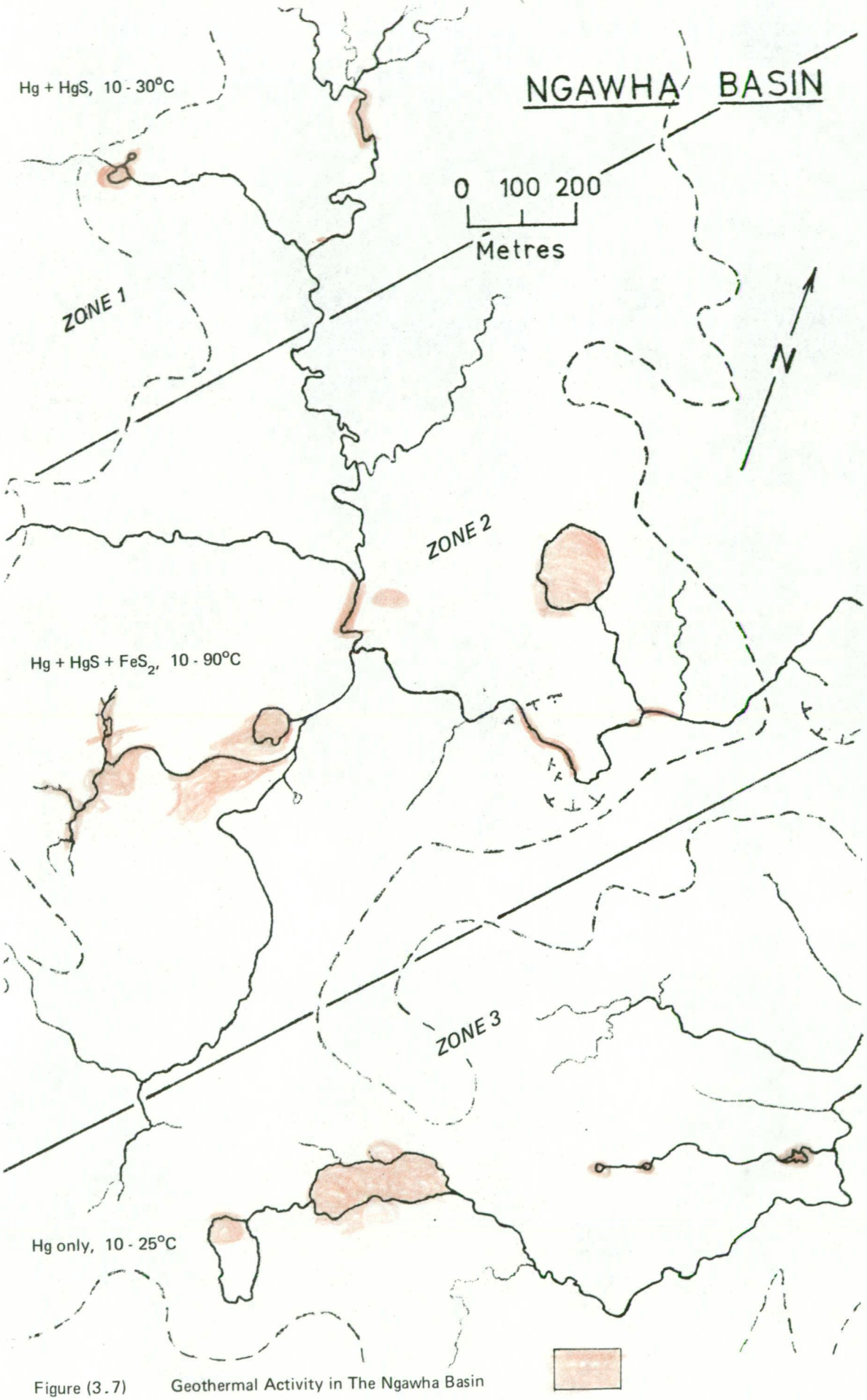


Figure (3.7) Geothermal Activity in The Ngawha Basin

associated erosion killed adjacent forest; however the outbreak of thermal activity was not explosive.

Activity has varied locally in the Ngawha region since first reported, but overall little has changed. There are some changes which indicate a distinct waning in activity sometime since the outbreak: Waiapawa, Little Waitetera and Waiparaheke Ponds have all been far more active in the past. The first two ponds were virtually inactive in 1976.

(3.5) GEOTHERMAL ACTIVITY

Within the basin all thermal activity is confined to three north-east/south-west oriented zones (Figure (3.7)). The zones are 0.2 to 0.5 km wide, one to two kilometres long and separated by one kilometre. Within the bands of thermal activity are ponds up to 350 m. All ponds more than four metres in diameter are cool to cold ($\leqslant 25°C$). Significantly raised temperatures are confined to the western ends of the northern and central zones: Waitotera Pond and the westernmost 650 m of the central zone. The largest thermal emanations are also in the western half of each zone, and the central thermal zone has the hottest, most widespread and most vigorous areas of all the geothermal activity.

Thermal activity manifests itself as gaseous emissions from dominantly muddy and sulphurous small pools. A few clear to faintly sulphurous pools with odourless gas percolation occur with less intense geothermal emanations. With the exception of one fumarole in Waiparaheke Pond, all large ponds have only weak to moderate gas emanating fumaroles ($\leqslant$ 500 ml gas/min.). Where fumaroles are hot ($\geqslant 40°C$) oil and tar are commonly present (Figure (7.5)), and the associated waters are least acid (pH 4 - 7).

Water discharge from springs is very small ($<$ 10 ml/sec each), whilst gas discharges are commonly two to three orders of magnitude higher. (Flows for waters in pools and streams are recorded in Table (A.20), and gas flows and their temperatures are given in Table (A.16). During prolonged dry periods the entire water run-off from the most active thermal zone falls below 750 ml/second (measured in May - June 1973). Most 'springs' are dominantly ground-water filled hollows with a minor geothermal influx of water. The pools are percolated by gas and undergo very considerable evaporation. (Evaporation is indicated by the D/H and $^{18}O/^{16}O$ study of McDonald (1966)).

Maximum surface temperatures are about 45°C in several small pools (e.g. Jubilee and Tiger Baths, see Table (A.20) and Figure (3.8)). Near the bottom of hot

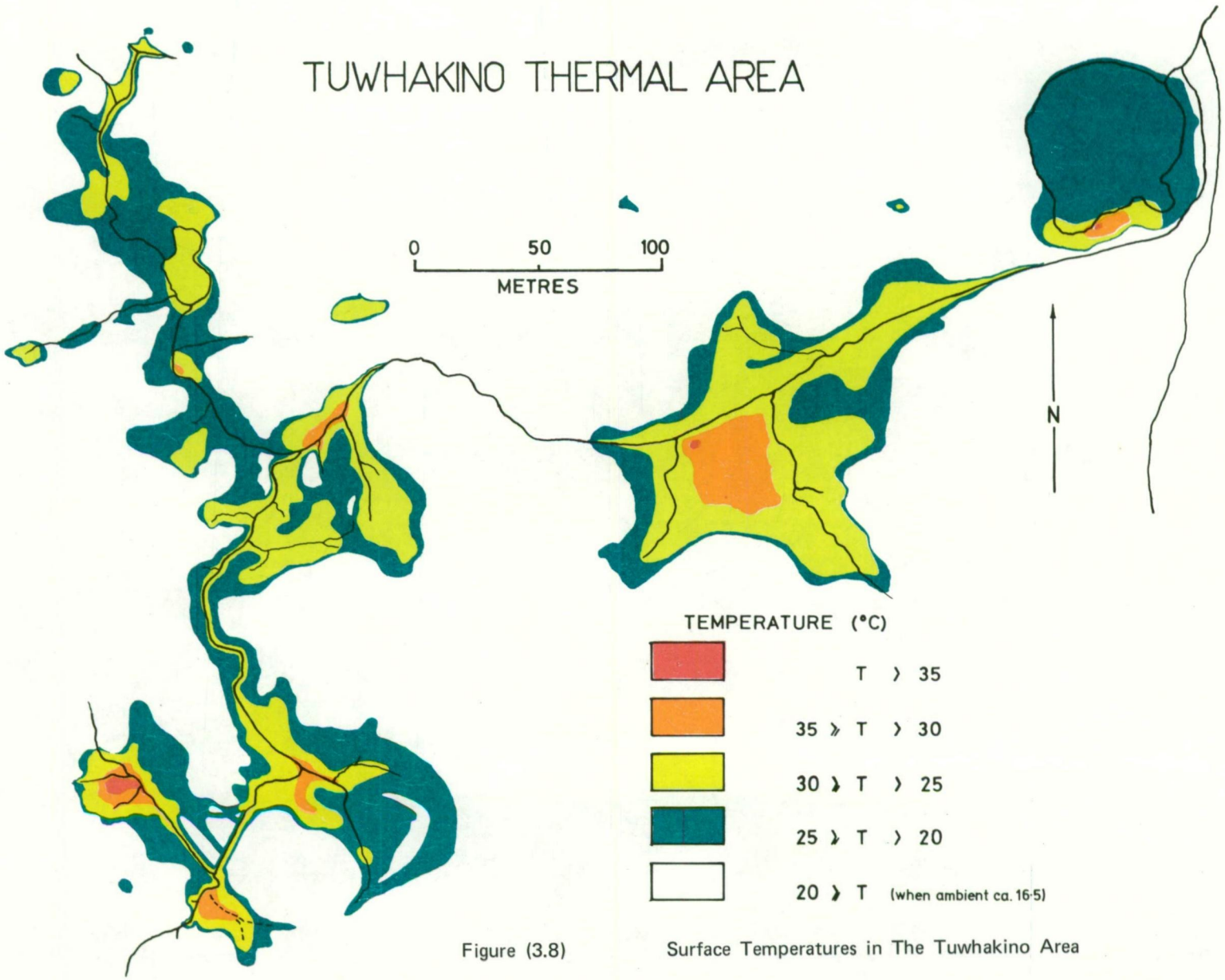


Figure (3.8) Surface Temperatures in The Tuwhakino Area

pools temperatures of about 60°C are common, and very rarely 80 - 90°C. Several centimetres below the surface, ground temperatures up to 50°C are common near hot pools, and one of 90°C was recorded 15 cm below the surface near the Tiger Bath in 1973. Surface ground temperatures are only high near the hottest pools and gas vents and are very much lower by one metre from hot emanations. No near surface temperatures above 35°C are found outside zone two (Figure (3.7)), and in zone three temperatures are rarely more than 5°C above ambient.

The thermal gradient below the Ngawha Basin is very high for the first several hundred metres and is probably linear (Figure (3.9)). It ranges from 350° C/km along the northern perimeter of the basin to about 615°C/km below the upper Tuwhakino area (Banwell, 1965). The CO_2 - rich waters are thus just below boiling-point for the hottest parts of the central thermal zone when and where pool-bottom temperatures are ca. 90°C.

Shifts in thermal activity have occurred, both recently and over the period since emanations first erupted. In all three thermal zones the eastern activity is weaker than that in the west: it is most obvious in the northern and central thermal strips where thermal emanations in the eastern half are almost extinct. More vigorous activity has occurred in the past and is evidenced by the presence of more sulphur in older sediments, the depth of the pools and the scores of buried trees near the base of the geothermal sediments. Currently hot thermal activity is confined to the western side of the zones. In the central zone slow undercutting of the ground along the western extremities is occurring in a few places, especially near the Tiger Bath (site no. 40 of Table (A.5)). Hence a north-east to south-west shift in activity is taking place.

The most prominent mineral associations of the thermal areas involve cinnabar, marcasite, haematite, elemental mercury, sulphur, alunite, tar and oil, with temperatures $\geqslant$ 30°C and H_2S - rich gas. Figures (7.8) and (7.9) show some of the common associations. Generally sulphur is more abundantly precipitated in cold H_2S - rich gaseous pools and stream beds although it is rare to find thermal emissions without detectable H_2S ($\geqslant$ 0.005 ppm) and precipitated sulphur. Hydrothermal iron minerals are restricted to fumarolic areas adjacent near-surface occurrences of basalt as are minor occurrences of antimony and copper concentrations in sediments.

Detectable anomalous elemental mercury is present in nearly all gases of the basin and pervades the soils and rocks for some distance (200 - 500 m) about each thermal zone. (Tables (A.2) and (A.3), and Figure (9.3)). Adjacent many warm fumaroles during cold weather films of elemental mercury develop (Figure (7.11)) and the element is readily detected in most gases by placing copper in the path of the gas.

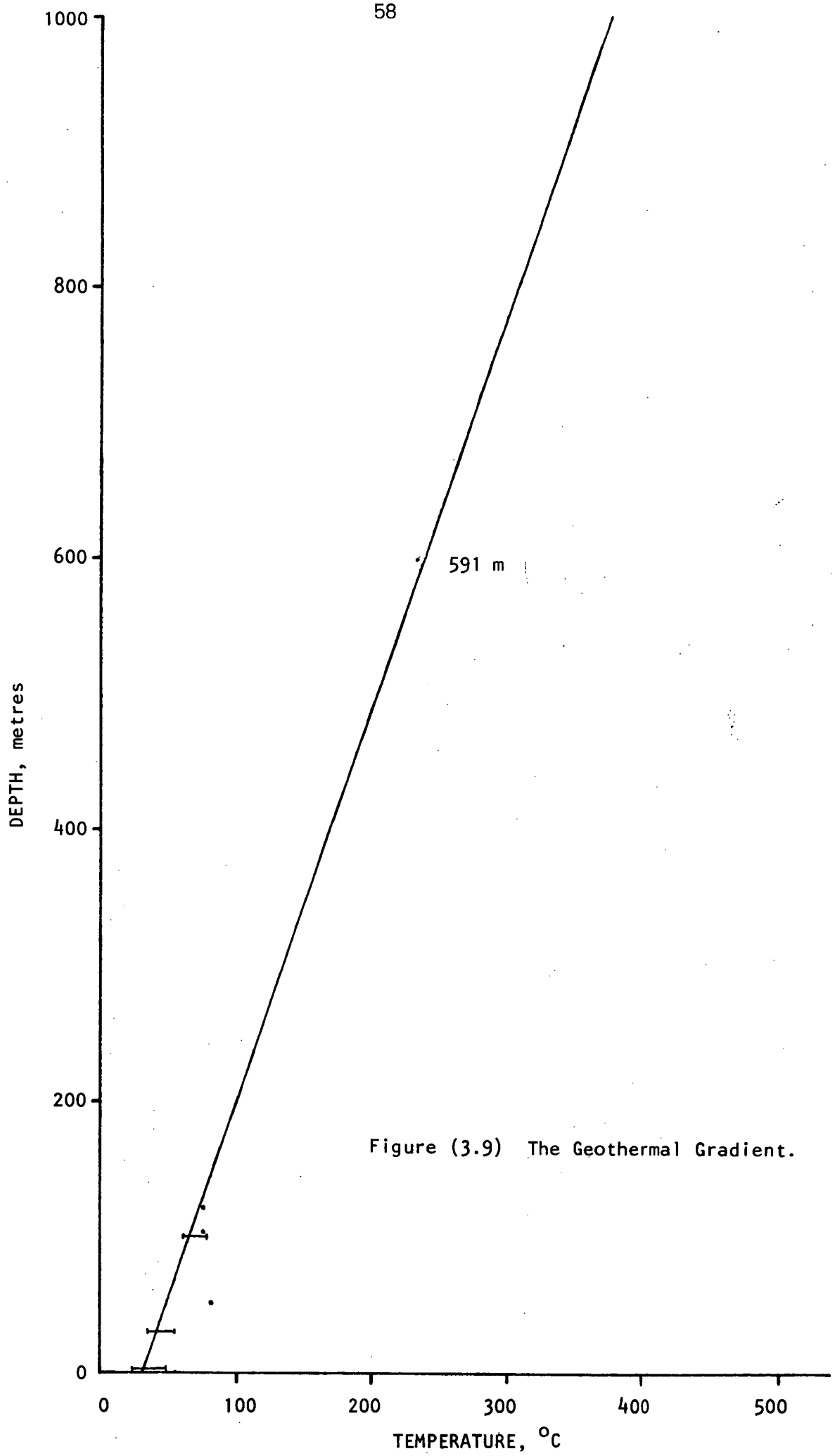


Figure (3.9) The Geothermal Gradient.

The absence of detectable anomalous mercury is virtually confined to gas percolating through large bodies of open water or running fresh water.

Visible cinnabar only occurs in the warm parts of zones one and two in spite of the presence of mercury-bearing fluids in all three zones (Table (A.20)). Cinnabar is also most abundant in the central thermal zone as are elemental mercury and iron sulphides, consequently all mining and commercial use of the thermal activity has also been restricted to zone two.

In accordance with the low temperatures silica sinter is rare. The few reports of relatively common sinter in the past are probably due to misidentified alunite, which is more common. Alunite bonds exposed geothermal sediments into hard crusts in most areas of warm to hot thermal activity.

(3.6) THE DEPTH OF THE MERCURY ANOMALY

The depth to which the mercury anomaly extends is where the hydrothermal leaching process begins and 'adsorption' mercury ends, which is where geothermal fluids are just 'part' of the hydrothermal convection cell and neither fugitive from it nor drawn into it. Below areas of vigorous thermal activity fluids escape fastest from the hydrothermal convection cell (or reservoir) and hence best represent the average convecting fluid(s). Assuming that the rate of migration from the cell is fast enough, equilibria established by the cycling fluids will be little changed in fast flows of deep geothermal fluids.

Accepting that the temperature of the convection cell can be calculated from isotope temperatures, the D/H isotopes ratios (Giggenbach and Lyon, 1977) suggest an average lower limit of about 215°C for the cell temperature which averages, ca. 250°C. Consequently 215°C is taken to represent the upper edge of convection cell and hence represents the limit of mercury extraction into the geothermal fluids which deposit mercury at the surface. The average ambient surface temperature is close to 15°C, hence the depth of the cell is readily calculable from the 200°C temperature difference and the thermal gradient (ca.400°/km average for the basin).

CHAPTER FOUR SOILS

(4.1) THE SOILS

The main reason for studying the soil was to investigate the concentrations of mercury present and correlate any significant variations with soil-type, horizon and bedrock(s). Based on the study anomalies may be recognised, hence the total quantity of mercury in the subterranean environment may also be calculated. To facilitate the above objective soils were classified by easily recognisable field traits suitable for differentiating anomalous mercury.

The damp warm temperate climate facilitates fast weathering under acid leaching conditions, which leads to podzolization or peat formation. Thus in spite of the young age of most of the basin soil development is relatively good; i.e. all the expected horizons can be distinguished in most profiles. The area without soil development is small, less than 0.5 km^2: it consists of geothermally active ground (ca. 0.365 km^2), water courses and a landslip.

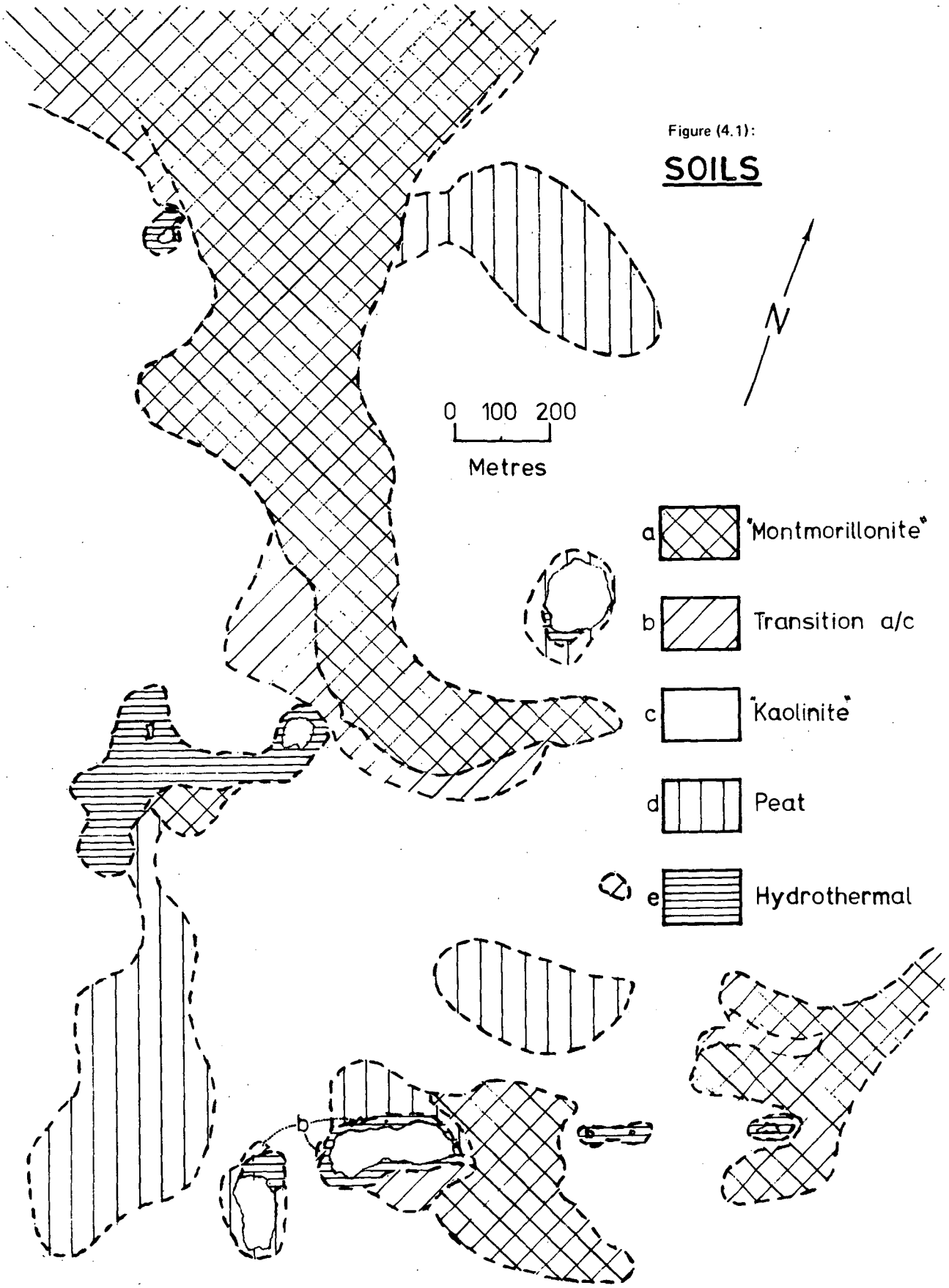
Figure (4.1) gives the distribution of soil-types. The soil of the basin is dominated by three types, which have been called:

(i) Kaolinite soils,
(ii) Montmorillonite soils and
(iii) Peat soils

for ease of campatability with field characteristics.

These soil-types are readily distinguished by the colour of the horizons from the leached horizon down to the weathered rock layer. The profile colours reflect the bed rock. The yellow-brown 'montmorillonite soils' occur only over basalt, the pale (almost white) 'kaolinite soils' occur over both the chaos breccia and the lake sediments. The bed-rock is also strongly reflected by the soil development: lake sediment profiles contain conspicuous quartz grains, common suggestions of bedding and the soil depth rarely exceeds 60 cm. Soil on chaos breccia is rarely less than 150 cm deep, lacks any suggestion of bedding or visible quartz grains, and may display evidence of ground movement. Peat occurs over lake sediments where drainage is poor and rarely extends as a fringe over basalt adjacent thermal activity. Peat soils once covered much

Figure (4.1):


SOILS
N
0 100 200
Metres
a "Montmorillonite"
b Transition a/c
c "Kaolinite"
d Peat
e Hydrothermal
b

of the basin, consequently old peat may be found in all modern soils except directly over the breccia. (The old peat is excluded from the classification of the currently forming soils.)

(4.2) SOIL PROFILES

The upper-most layer of a modern soil consists of a mat of plant debris grading downward into a mixture of decomposed organic matter and weathered parent material. As water filters through the decomposed organic matter, various organic acids are formed and carried downward into the layers below, where they react with and alter the mineral matter. Some of the products of alteration are soluble and are moved downward in solution. Colloidal material may also be moved downward in suspension.

Thus soil is composed of mineral and organic materials developed 'in situ' by physical, chemical and biological processes into organised profiles of more or less horizontal layers.

As a soil matures, various horizons (O, A, B and C) with different chemical and physical properties develop as shown in Figure (4.2). (Not all the layers depicted in the figure may develop in a soil).

(4.3) THE PROFILE DESCRIPTIONS

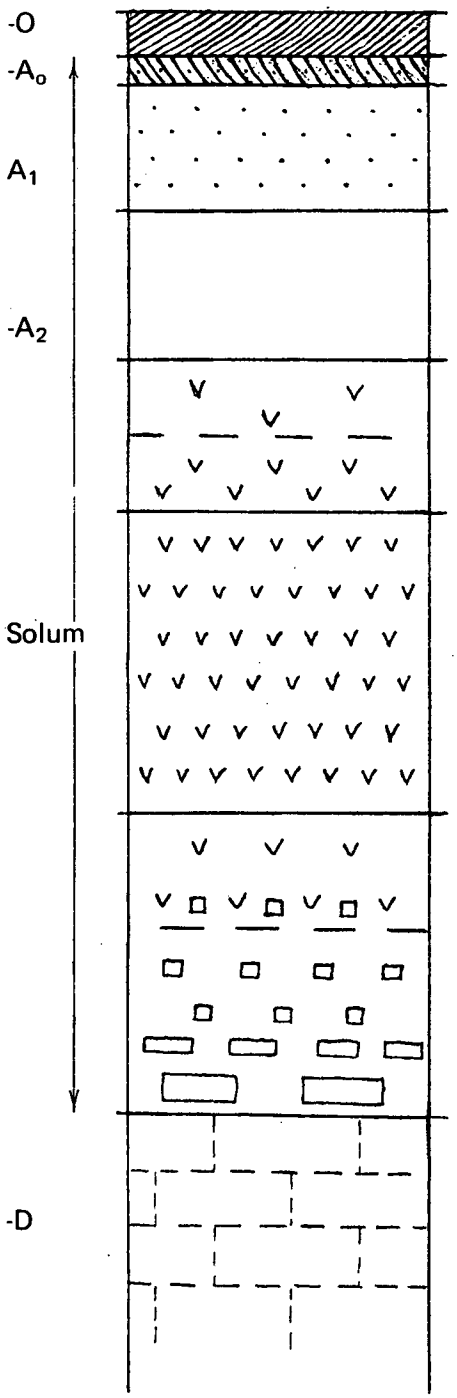
Each profile site has a two part description: the first is a general description of the profile locality, and the second describes the nature of the profile 'in situ'. The descriptions are included in the appendix.

The format of the first part is: - profile number, name[1] geographical co-ordinates[2], relative elevation[3], parent material and form, slope, erosion, ground-water, geothermal activity, vegetation and human influence. Following this there may be a further comment on the area.

The second part is the description of the horizons in order of depth. In some instances the horizon thickness and depth are so variable that the approximate average depth interval is given. The descriptions include consideration of the following properties: thickness, moisture content, colour[4], mottling, stains, composition, sorting,

Figure (4.2)

HYPOTHETICAL PROFILE



Horizon		Description
O	-	Litter
A_o	-	Organic Layer
A_1	-	Organic-rich A Layer (Maximum biological Activity).
A_2	-	Maximum Leaching (Mineral Layer)
A_3	-	'A' gradational with 'B'
B_1	-	'B' gradational with 'A'
B_2	-	Maximum Deposition (clay, humus, iron)
B_3	-	'B' gradational with 'C'
C	-	Weathered Parent Material (geologic, not pedalogic organisation).
D	-	Fresh Parent Material (Rock, transported material or former soil).

shapes of grains, grain size, homogeneity, structure, compaction[5], rooting, hardness/firmness, fissility, plasticity, stickiness, porosity, permeability, odour, temperature, pH, gas, hydrothermal minerals and boundary nature. Where a comment is irrelevant, it is usually omitted: i.e. the property may be assumed to be 'absent' or 'normal': e.g. ambient temperature.

a. General Vegetation Description

The main natural vegetation in the basin is juvenile tea-tree scrub, dense gorse, bracken, swamp grasses with sparse tea-tree, agricultural grassland and very rare juvenile to submature kauri rain-forest.

In small sheltered areas the vegetation is thickest and is usually dense tea-tree scrub and rarely juvenile rain-forest in steep gullies. In general the vegetation is of poor quality.

b. Profile Characteristics

The young age, the low relief, the lack of microclimates, and the simple geology of the Ngawha basin give rise to poorly and similarly developed soils which reflect the local history and the bedrock (c.f. Figures (3.3), (4.1), (4.3) and (4.4)).

The depth of weathering is small (< 2 m) over the lake sediments and basalt, although it may be large (≥ 3 m) near thermal zones due to supplemented alteration by adjacent geothermal emanations. By contrast weathering of the chaos breccia is deep usually, and top-soil development is poor.

Profiles of four main kinds are present, each of which depends on the parent bed-rock, these are:

1. Basalt (montmorillonite soil)
2. Chaos Breccia (kaolinite soil)

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1. The name given is not necessarily that of the site, but that of the local region since most names refer to water bodies and thermally active sites.

2. The co-ordinates are those as read directly from sheet 15 of Gough (1965).

3. The relative elevation has been calculated using Fleming's map (1945) where he took a point at the south-east corner of the Spa Hotel to be 450 foot A.S.L. and used it as his origin. (This is about 29 m less than that implied by the far coarser scaled 'Sheet 15' in 2 above. The sheet is useless for accurate work except for the direct use of the Trigonometric Points listed).

4. Colours as named by the Japanese Ministry of Agriculture.

5. Compaction refers to the relative efficiency of packing of the constituents in a particular horizon. Very good compaction means that the material cannot be 'compressed' any further without breaking of the constituents particles. Such a material may be either porous or non-porous; e.g. well sorted coarse-grained material will be quite porous, and is usually very permeable to fluids.

Figure (4.3) Schematic Geology Profile of The Ngawha Basin

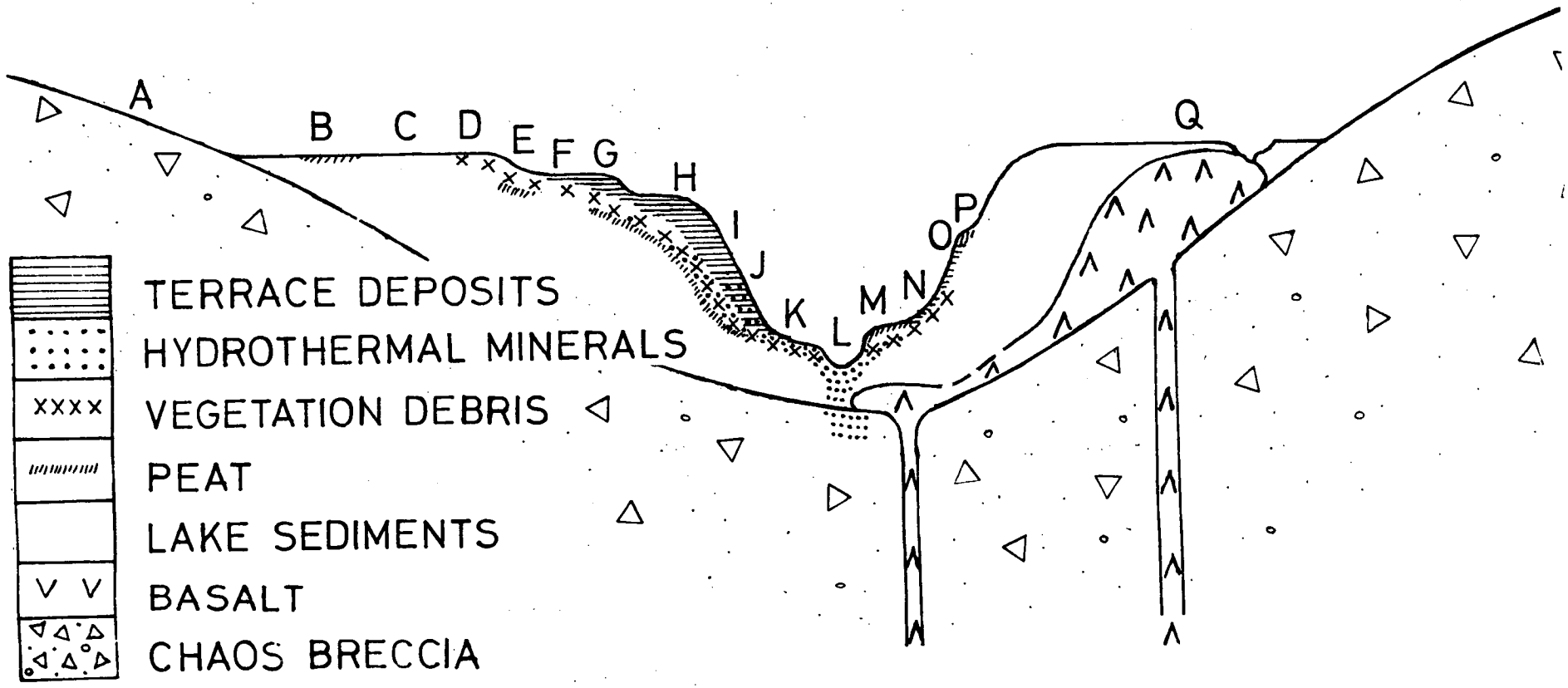


TABLE (4.1) PROFILES OF THE NGAWHA BASIN

All profiles listed below are depicted in Figure (4.3) and detailed descriptions for examples of each are given in the appendix.

A	Chaos breccia
B	Thin peat / lake sediments
C	Lake sediments
D	Vegetation debris / lake sediments
E	Vegetation debris / peat / lake sediments
F	Terrace sediments / vegetation debris / lake sediments
G	Terrace sediments / vegetation debris / peat / lake sediments
H	Terrace sediments / vegetation debris with hydrothermal minerals / peat / lake sediments
I	Terrace sediments (some have stream sediments also) with hydrothermal minerals in lower part / vegetation debris / peat / lake sediments
J	As above but no peat
K	Terrace sediments rich in hydrothermal minerals / vegetation debris (commonly charred) / lake sediments
L	Stream or pool sediments rich in hydrothermal minerals / disrupted lake sediments with a high hydrothermal mineral content near vents.
M	Peat / vegetation debris with minor hydrothermal minerals / lake sediments (possibly some peat in upper part)
N	Terrace sediments overlying the above
O	Peat / terrace sediments / vegetation debris
P	Peat / terrace sediments (or less commonly as for N)
Q	Basalt (some have minor lake sediments in the upper horizons)

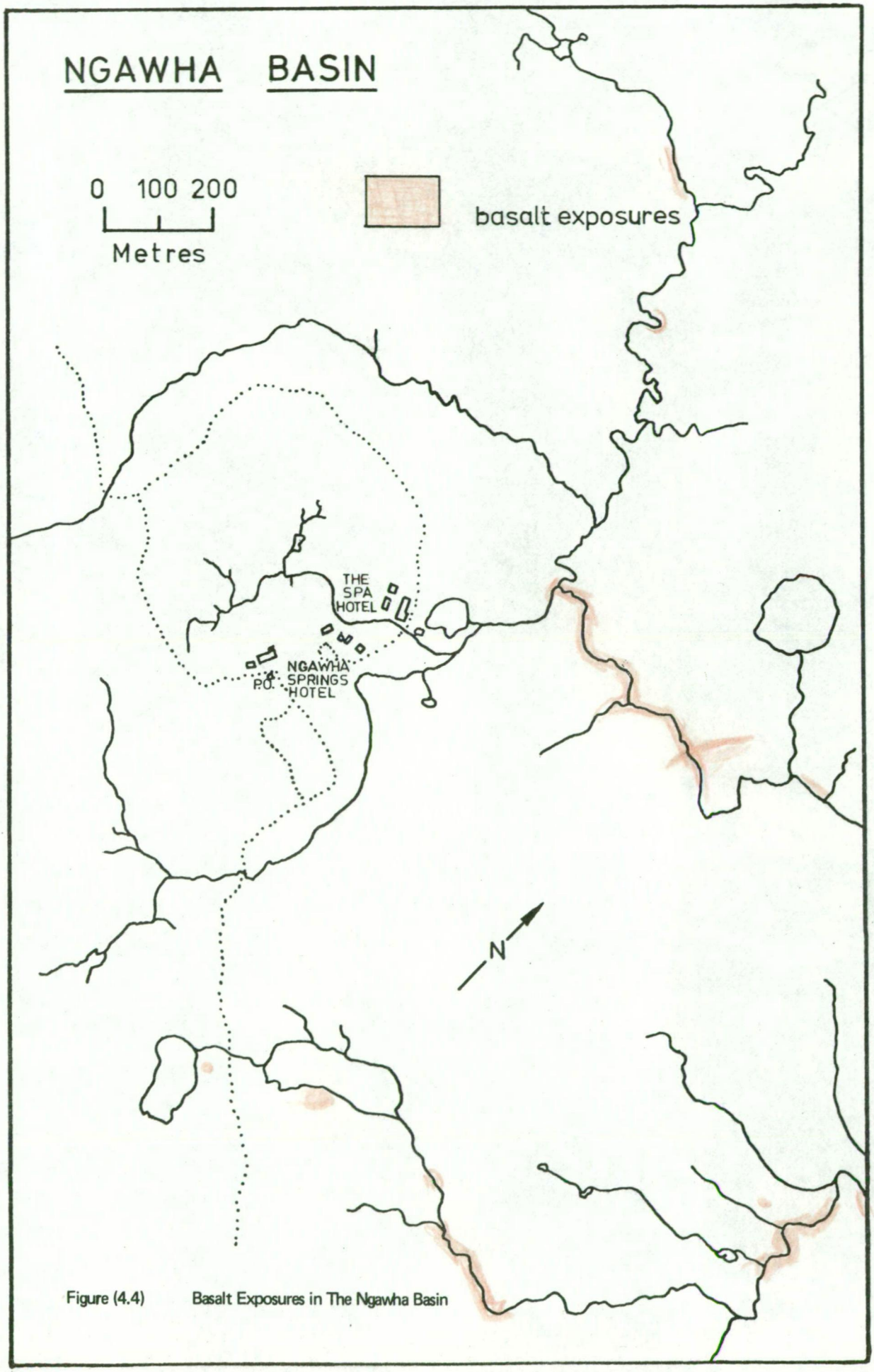


Figure (4.4) Basalt Exposures in The Ngawha Basin

3. Lake Sediments (kaolinite and peat-soils)
4. Geothermal Sediments (usually no soil)

The soil profile development related to each is given in Table (4.1).

(4.4) BASALT

Basalt occurrences are shown in Figures (3.3) and (4.4), but soils which reflect the presence of basalt are considerably more restricted (Figure (4.1)). The rock outcrops in several spots along the Te Pukoro - Ngawha Stream and the Mangatawai Stream, with other small natural outcrops near Waiparaheke and Ngamokaikai Ponds.

Erosion is minimal compared to other rocks, even where the water has cut 6 metres into adjacent rocks: rarely is there more than 0.5 m cut into the basalt.

Characteristic of the profiles is the shallow depth to bedrock, the relatively intense colour (due to iron) and good top-soil development. The bedrock is usually less than 0.75 m depth, otherwise lake sediments tend to dominate. The surface of all the normal/typical profiles are close to the level of the basin plain. Below the organic horizon the entire profile is strongly 'iron' coloured (various browns) unlike the profiles above other bedrocks. There is a complete lack of sandiness, bedding (or banding) and mottling. All the horizons merge, however each is readily distinguished by colour and 'feel' (firmness, crumbliness and plasticity). The clay is montmorillonite, and does not occur elsewhere in the basin. A few clayey horizons over lake sediments are very similarly coloured (dull yellowish brown) but are readily distinguished by their sandy feel. All other clay is much paler.

The shallow depth of the bedrock confirms the young age(s) of the basalt(s). Deep profiles occur in the fault zone near N15/377350, where earth flows are common, and between the Tuwhakino Stream and the main part of Ngawha Springs, where pyrite may occur in the basalt (Jones, 1939).

(4.5) CHAOS BRECCIA

The chaos breccia forms the bulk of the bedrock surrounding the lake sediments (Figure (4.3)). However, due to the deep weathering fresh outcrops are rare and temporary. They are only found where there are massive earth flows, and all but one of the flows lie outside the original perimeter of the lake sediments.

A

B

C

Figure (4.5) A: Limestone boulders from the chaos breccia eroded by the Ngawha Stream at N15/358350. B: Typical land-slips in the chaos breccia. (The gorse in the Foreground is 2.5 m high). C: Profile A, the top half, 1/8x. The top is a crust of mainly alunized coarse-grained sediments which contain minor cinnabar. The top of the geology pick rests on a carbon dated tree, 6850 Y.B.P.. The geothermal sediments have a dip of about 20 to 30 degrees which there has been some movement of them during the last few thousand years, possibly due their undercutting by ebullient removal of local sediments..

In fact the chaos breccia is characterised by earth movements (Figures (3.6) and (4.5)).

The breccia has deep weathering (most $\geqslant$ 3 m), very poorly developed top-soil on massive, almost white kaolinite, and many slips in undulating and hilly country due to its incompetence. None of the other parent materials are so deeply weathered: the minimum depth to fresh breccia is ca. 250 cm, whilst the maximum depth to fresh rock is less than ten metres except in thermally active areas. The massive kaolinite alone is sufficient to distinguish the profile parent material. (Kaolinite is only present as a mixed constituent in the lake and thermal zone sediments). Rarely does the chaos breccia show good soil development: organic and organic rich horizons more than a couple of millimetres thick are restricted to a few sheltered valleys. The poor vegetation and scattered showings of 'kaolinite' contrasts that over basalt and lake sediment profiles.

(4.6) LAKE SEDIMENTS

The sediments cover the bulk of the basin and are directly below most areas lying in the plain of the basin. No natural outcrops exist. The sediments are poorly consolidated and show no sign of diagenesis, consequently they are easily eroded. Weathering is relatively slow because of the very high quartz content. As a result the top-soil is not deep although it is commonly well developed apart from abundant quartz in all but the litter horizon.

The sediments are characterised by the silty/sandy nature of all horizons, and the presence of considerable parent or weathered parent material in the deposition and some leached horizons. Consequently the two horizons are more strictly part of the weathered parent material where they are bedded and the deposited material is interstitial. (Bedding is not present in the basalt or chaos profiles, it is common in the thermal zone sediments). The profile-type only occurs where the ground surface is about level with the basin. Peat is present (over the sediments) in shallow depressions, poorly drained flats, and at the edges of most thermal depressions where it may extend down over terrace deposits. The presence of basalt less than five metres deep causes the lake sediments profiles to be browner than the usual dull yellow oranges to light greys of the leached zone and below.

(4.7) THERMAL ZONE SEDIMENTS

The sediments lie within the depressions about thermal activity and are not the normal undisturbed lake sediments. The thermal zone sediments are chiefly derived

Profile Descriptions Summary

TABLE (4.2)

	BASALT A (Q)*	CHAOS BRECCIA B (C, U)*	LAKE SEDIMENTS C (N)*	THERMAL ZONE D (A, D, F)
LITTER 0	0.4 - 1.5 cm deep Distinct definition Healthy vegetation, fairly dense litter accumulation and entire ground covered.	0 - 0.75 cm, normally $<$0.3 cm Distinct when present, only scattered leaves in other areas. Vegetation is commonly stunted. (In some steep sheltered valleys litter is up to 7 cm)	0.3 - 2.0 cm deep Distinct Healthy vegetation except near sulphurous or peaty ground (Where always moist may merge into A_o)	0 if mineralised No vegetation, rare litter (If vegetation is growing, profiles are akin to 'lake sediment' profiles).
ORGANIC A_o	0.2 - 3.5 cm thick Distinct definition Well rooted, soft, damp very porous, matted Brownish black merges into	0 - 0.5 cm thick usually absent except in some sheltered valleys: 1 - 2 cm	0.2 - 3 cm commonly $\leqslant$1 cm Distinct band, narrow and continuous. Characteristically black rapid change to	0 No modern organic matter (May contain ancient vegetation debri or peat up to 40 cm deep, very rarely to 150 cm depth).
ORGANIC RICH	0.75 - 15 cm, commonly $\geqslant$3 cm Well defined, transitional base, well rooted, fibrous top Brownish black to dark greyish yellow	0.2 - 3.5 cm thick, rarely $\geqslant$2 cm Indistinct due to low organic content. Some with weakly fibrous top, light grey to brownish greys, very clayey. Fades into leached zone.	0.5 - 10 cm thick Distinct or thick merging base, brownish black to dark brown, very sandy feel, crumbly, no plasticity merges into	0 No modern organic matter. (Commonly no equivalent present)
LEACHED A_2/B_1	5 - 40 cm thick Transitional boundaries well characterised by dull yellow to dull yellowish brown clay. Rarely brown. In lower part of thick horizons good compaction.	30 - 80 cm thick Well defined; traditional or abrupt boundary. White to light grey clay, firm (Can be outcropping at slips)	10 - 40 cm thick Transitional Vague bedding in some areas. Commonly very porous. Dull yellow orange.	0 - 60 cm only at relatively elevated si Common at exposed inactive localities containing dominantly coarse-grained sediments (Essentially the iron and sulphur minerals are absent). Can have cinnabar.
DEPOSITION B2	8 - 25 cm thick Gradual to rapid mergence above, abrupt below. Bright yellowish brown to yellowish brown. Firm to stiff clay.	30 - 250 cm thick Variable definition, tends to be vague Dull to light yellow orange. Dominantly clay with pale mottly iron stains rare columnar kaolinite.	10 - 35 cm, irregular thickness Always ill-defined, transitional between above and parent. Vague to well-bedded. Deposition is interstitial. Some brownish grey organic stains.	0 - 125 cm Only in elevated inactive areas, has interstitial limonite, alunite and rarely sulphur or pyrolusite. May merge with the above or contain pockets of it.
WEATHERED PARENT 'ROCK'	0.2 - 2cm usually $<$1.25 cm Distinct, not separate from parent mass Yellowish grey, ca. Fissile and firm. Similar texture to parent.	50 - 300 cm can exceed 500 cm Irregular boundary, variable definition, tends to be sharper at base. Distinguished by breccia texture. Colour varies from above to mostly brownish greys. Limestone boulders persist if present below.	10 - 20 cm thick Bedded: from vague to distinct and fine-structured at depth. Slow mergence to parent rock. Commonly hard to differentiate from parent rock.	15 - 300 cm, mostly $\leqslant$100 cm Elevated inactive areas plus some low-lying areas. General alteration of FeS_2 to haematite or limonite pseudomorphs. Tends to occur in moist ground.
FRESH PARENT ROCK	From 15 - 85 cm depth Impervious to gas and water. Where below 75 cm, lake sediment profile transition in upper part.	Starts below 150 to 600 cm. Grey, incompetant, and impervious to water over several metres.	Usually between 20 to 80 cm thick Porous, permeable and pale; browner where close to basalt.	Unaltered 'thermal' sediments occur below 10 - 125 cm. Matrix is mostly reworked lake sediments, minor clay fragments are present locally. May contain sulphides.

* Examples of some typical profiles given in the appendix.

from, and overlie the lake sediments. Stream, pool and lake sediments, terraces, mounds, mineralized bodies and fumerole margins in thermal areas are formed by the thermal sediments.

The profiles vary considerably, however all but some terraces lack soil development. There is broad-scale differntiation (by component bedding representative of historical events (Figure (4.3)). Superimposed on the differentiation is weathering which gives rise to conspicuous characteristics in mineralized zones.

The profiles in non-mineralized areas are very similar to those for lake sediments; for example low-lying terraces commonly have peat profiles. The profiles are more juvenile and a band of forest debris is very commonly present.

In the low-lying non-vegetated zones the profiles have a dry to damp crust of cemented sediments above water-saturated, uncemented and relatively anaerobic sediments. Where the surface is wet the crust is usually missing. Below the two layers is one rich in organic debris (leaves, logs and possibly minor peat) above another layer, which is peat or peat-rich and overlies almost normal lake sediments which may contain minor elemental sulphur and stains of iron mineralization. Thermal activity usually breaks out once the superficial sediment crust is penetrated (warm water and gas flows which increase with depth).

The thermal areas (mostly terraces of the formerly larger pools) have very little soil development even where tea-tree now abounds. Many terraces have a surface or near surface peat horizon of ca. 10 - 25 cm thickness over bedded sediments. Redeposited material composes the terraces, and tends to have a small increase in grain-size with depth. This matrix continues until it is dominated by vegetation debris which yields to peat overlying lake sediments. In a given depression the lowest level of the 'in situ' crusted thermal sediments usually marks the first appearances of significant hydrothermal minerals in association with terrace sediments and other materials. Commonly fluvial erosion of the terraces causes a considerable quantity of the later mineralization to form in lower parts of the depressions where the greatest concentrations of thermal emissions are.

There is a general increase in total hydrothermal mineral concentration with depth until a sharp cut-off close to the base of the vegetation debris. The major exceptions are the orifices of large vents where hydrothermal minerals penetrate much deeper in and about the vent. Where it was possible to dig to 'standing' ground-water below high terraces thermal activity broke out similarly to that in low-lying areas. At this

A

B

C

Figure (4.6) A: Near profile E; note the geology pick on the protruding layer of organic debris. incorporated into the terrace sediment base which lies above the lake sediments. The lake sediments here do not show any fine bedding due to disturbances by once active gas emanations. B: The dark band corresponds to the period when thermal activity first broke out, it is organic-rich and separates the lake sediments (below) from the later thermal pool terrace sediments. C: Sulphur bands in terrace sediments which overlie the lake sediments (at bottom right), 1/30x.

(water) level there is commonly an increase in vegetation debris and hydrothermal mineral concentrations (e.g. profile D), and metallic mercury and H_2S were readily detected.

The highest terraces, which have formed close to the edge of the original lake basin surface, may have considerable piles of vegetation debris just below the present ground surface (e.g. profile J) (Figure (4.6). Thicknesses up to 2.5 m were found overlying pelitic lake sediments and intermediate veneers of terrace deposits.

(4.8) RECENT GEOLOGICAL HISTORY

The recent geological history of the Ngawha Basin is well preserved by the stratigraphic successions in the profiles. Most conclusions are compatable with those of Bell and Clarke (1909). The main exception is their suggestion that thermal activity broke out explosively.

Bell and Clarke do not report any soil examination, nor any events subsequent to the outbreak of thermal activity. Their relevant conclusions were summarised on page 258 in Fleming's paper (1945). Fleming briefly discussed the physiography of the Tuwhakino thermal area and concluded that there were seven levels of still-stand as the area drained to its present levels. Apart from these studies and the drilling by mining companies, little other relevant study on the soils has been made.

Figure (4.3) shows an exaggerated-scale profile across the basin constructed from profile studies.

Assembling the profile horizons in a chronological sequence the following events in order of decreasing age are established:-

a. Basalts flowed into the valley and dominantly followed the water-courses (Jones, 1939; Skinner, 1966). A basalt flow dammed the valley (Bell and Clarke, 1909) post 40,000 Y.B.P.

b. Drowning of a kauri forest was followed by ca. 10,000 to 15,000 years of lacustrine silting. The silt came from the local hills.

c. The lake broke out to the east along two low saddles (Bell and Clarke) before 15,000 Y.B.P. when a forest had regrown in parts of the basin. Large areas of the basin also began forming peat.

d. Down cutting of the streams draining the basin followed in stages according to the ease of erosion of the saddles (Fleming, 1945).

e. Thermal activity broke out at ca. 6,900 Y.B.P. and caused catastrophic collapse of forest locally (induced by ebullient sapping of stream banks). Hydrothermal minerals begin to appear in stream and pool sediments.

f. Pools formed by ebullient erosion begin partial silting and terrace formation with relatively coarse materials including peat, vegetation debris and hydrothermal minerals.

g. As further entrenchment (0.6 to 3 m) of streams occur, low-lying terraces become vegetated and start forming new peat. Exposed areas of sulphide mineralisation are weathered, leaving cinnabar and removing the iron sulphides. Forest covered most of the valley.

h. During the last half of the century nearly all the forest was removed by man.

i. Between 1895 and 1934 most of the economic cinnabar occurrences were mined. Minor water-course excavations were done to increase drainage.

CHAPTER FIVE ANALYSES

Mercury analyses were mostly done via cold vapour atomic adsorption, and some by use of the electron micro-probe. All other chemical composition determinations were done using standard X-ray fluorescence techniques and the electron micro-probe, a few sulphur determinations were done gravimetrically. Carbon forteen dating and mercury isotope determinations were done by the Institute of Nuclear Sciences, Petone, New Zealand and the Chemistry Department, University of Tasmania respectively.

(5.1) MERCURY

Elemental mercury vapour so strongly absorbs light of wavelength 253.7 nm (the molar extinction coefficient is 4.1×10^6 cm^2 mol^{-1}) that very small quantities of mercury can be detected using the property. Hence by extracting the mercury from a sample and reducing it to the element, the concentration of mercury in the original sample may be calculated. Many procedures using the absorption property have been developed in the last 15 years (Brandenberg and Baden, 1965; Hatch and Ott, 1968; Stainton, 1971; Weissberg, 1971; Hoggins, 1972; Long, Scott and Thompson, 1973 and McNerney and Buseck, 1973).

In this work a method paralleling that of Hatch and Ott (1968) and Stainton (1971) was used. The method of Long, Scott and Thompson was tried: collecting mercury on silver, but it was not successful due to considerable difficulty with H_2S 'poisoning' the silver at Ngawha Springs.

The samples were dissolved in acid-oxidizing solutions which cause total destruction of the sample, and the mercury so dissolved was stored in the digestion solution until analyses. A 5 ml aliquot of the digested sample was put into a 100 ml container attached to the atomic absorption apparatus, and 10 ml of a reducing solution was added and shaken to reduce the mercury to the element and equilibriate the vapour with the enclosed air. The airborne mercury vapour was then pumped through an absorption cell for analyses (Figure (5.1)).

The analysis instrument is the 'Mark 1' model mercury detector built by 'Tasmanian Technical Services Pty. Ltd.' It has an inbuilt pump and a small vapour by-pass to prevent fogging of the absorption cell. The tubing in the machine was replaced periodically to keep background mercury levels as low as possible.

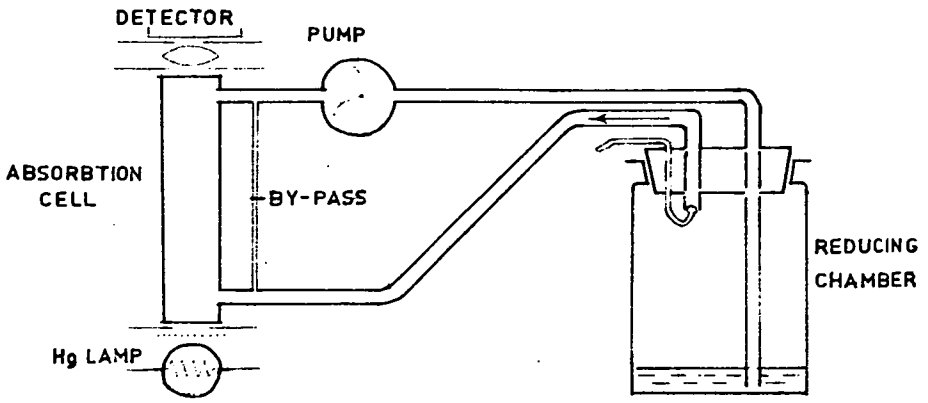


Figure (5.1) The Cold Vapour Atomic Adsorbtion Line

With normal careful use the instrument could detect about 0.5 ngm of mercury. For results to have a relative standard deviation of 5% or less, about 5 ng or more is required. For samples with too low a concentration for direct digestion and analysis, concentration of the mercury was achieved by adsorbing the digested mercury onto gold and leaching into a smaller volume of solution.

(5.2) DIGESTION OF SAMPLES

One of three digesting solution was used to dissolve each of the field samples:-

1. 10, 15 or 20 ml HNO_3 + 10 ml H_2SO_4 + 5 or 8 ml $KMnO_4$-saturated 2M H_2SO_4.

2. 10 ml HNO_3 + 5 ml 2 M H_2SO_4 + 5 or 10 ml 100 H_2O_2 + 4 ml $KMnO_4$-saturated 2M H_2SO_4.

3. 10 ml HNO_3 + 10 ml 2M H_2SO_4 + 20 ml 48% HF + 5 ml $KMnO_4$-saturated 2 M H_2SO_4.

In all cases, at the commencement of digestion, 1 ml of the $KMnO_4$-saturated 2M H_2SO_4 was added to each sample to make the digestion environment oxidizing in order to prevent the loss of mercury as Hg^o.

Just prior to digestion samples were broken up to allow ease of access to the acid solution. Only rocks and other completely solid samples were crushed by a ring mill. Silica and limestone were treated similarly to check for mercury gain and loss. (Limestone is also digestable without crushing). Results indicated no gain in mercury but possibly a small loss of about 5% on samples containing up to 0.5 ppm. The few samples containing more mercury (all sinters) may have lost 10 - 20% due to the presence of minor free cinnabar. Samples suspected of containing relatively high concentrations of mercury were always treated last, whether for crushing or digestion

to reduce contamination.

Digestions were carried out on 1 to 2.5 gm of sample in a 100 ml stoppered flask or teflon beaker with a snug-fitting lid. The reagents were added cold, slowly and intermittently in the order as shown above with constant swilling. Once all the reagent was present and the solution oxidizing and acidic, the mixture was left for two days and occasionally shaken and excess pressure released. Next the solution (and insolubles) was made up to ca. 45 ml and the stoppered mixture gradually heated to 100°C on a water-bath until complete dissolution. The sample was usually kept on the bath for at least two days. Afterwards it was allowed to cool and was made up to 50 ml. At the end of the heating process 1 gm of H_3BO_3 was added to the fluoride digestion to help remove excess fluoride before dilution to 50 ml.

Digestion solution number 1 was used on all samples possible: soils, limestone, animal material, gas, vegetation, minerals and colloidal sediments. The amount of nitric acid and permanganate were varied (as above) according to need to completely digest the solution in an oxidizing acid environment. Soil horizons and some sediments required the extra oxidizing reagents. The digestion technique was also used for the leaching of mercury from gold, glass and plastic, both for analyses and cleaning.

Digestion mixture number 2 was used on organic materials, mostly vegetation. The hydrogen peroxide was not added until about one day after the addition of the acids, otherwise excessive effervescence occurred. It was then added a few drops at a time every several minutes, with swilling and shaking. Most samples required a 10 ml aliquot.

Digestion mixture 3 was used on most rocks as well as many soil and sediment samples, plus the sinter samples.

a. Reagents

All reagents chosen were those which contained the lowest mercury concentrations from the commercially available analytical grades reagents. Only hydrogen peroxide had to be especially procured to sufficiently limit its mercury content. Water was distilled then treated by a deionizing resin to yield undetectable mercury under the normal conditions of sample analysis. The reductant which contained a significant concentration of mercury when freshly prepared readily lost its mercury by passing dry oxygen-free nitrogen through it until after no mercury was detectable. (The nitrogen was passed through a mercury trap of oxidizing acid mixture 1 then a clean gold filter).

Chemicals chosen for lowest mercury content were:-

nitric acid	hydrofluoric acid
sulphuric acid	hydrochloric acid
boric acid	stannous chloride*
hydroxylamine . HCl*	nitrogen*
deionizing resin	benzene*
cysteine. HCl	potassium permanganate
hydrogen peroxide	ammonium hydroxide
potassium dichromate	

* These chemicals were also freed from detectable mercury. Benzene was purified by simple concentrated sulphuric acid extraction, which presumably extracts any thio-species and hence the mercury.

(5.3) SAMPLING

These were collected to represent areas of geothermal activity and emanations mineral distributions, solution and sediment transport, and processes involved in cinnabar deposition. Sample sites are shown on Figures (A.1) to (A.13). The method for taking the various samples is indicated below.

a. Solids

Soils, minerals, sediments, rocks, animal and plant material are the chief solids. These were taken as a ca. 1½ kg samples (ca. 250 gm for plants). All were tightly packed into thick polythene bags which were made as air-tight as possible using two ties and often two bags. If low metallic mercury concentration was suspected a small sample was placed into an air-tight glass vial which holds ca. 40 gm of soil on gentle packing. High mercury content samples were packed together and low ones similarly to reduce spoiling.

When used in the laboratory material was taken from the centre of the bulk sample.

b. Liquids

Waters, oozes and some sediments fell into this category. They were put into 500 ml leached glass bottles or leached plastic bottles with lids and gaskets.

For waters the mercury was kept in solution by adding 20 ml of nitric acid and 1 gm of $K_2Cr_2O_7$. However to calculate free mercury in the water another sample had to be taken for the above technique gives the total mercury present since all the mercury becomes oxidized.

The methods used were:-

1. Collection of water and immediately treat with $HNO_3/K_2Cr_2O_7$.
2. A few drops of H_2SO_4, filter, treat with $HNO_3/K_2Cr_2O_7$.
3. A few drops of H_2SO_4, filter, blow off volatiles, $HNO_3/K_2Cr_2O_7$ treatment.

c. Gases

These were collected by local water displacement into 550 ml glass containers which were sealed by hot waxed rubber stoppers which were wired on then waxed again. However, due to the small amount of mercury expected, gases were slowly passed through an acid-oxidizing medium to extract the mercury. 18.5 cm high 500 ml leached polythylene bottles were four-fifths filled with a mixture 1 part 5M H_2SO_4 saturated with $KMnO_4$ plus 2 parts 60% HNO_3. Gas flow was controlled to a rate of one bubble per second into a constant depth (16.5 cm) of the acids. (Laboratory experiments showed that all the mercury can be extracted from the gas). Tubing was lagged and gas allowed to run freely for some minutes before connection to equilibriate the tubing surface with mercury and temperature. The apparatus was also kept as near the warmest spot as possible to reduce condensation. Outflow was separated from the atmosphere by a small air-lock and could be sealed off from the collector by a Hofman clamp. This allowed the solution to be shaken with the gas from time to time. Gas volume was monitored by water-displacement of the gas leaving the apparatus. (Only a very minor percentage of the gas reacts in the system; mostly NH_3, H_2S and mercury). The gas flow was stopped before the permanganate colour disappeared.

(5.4) MERCURY SPECIES

a. Cold Extractable Mercury

The sample is treated with digestion mixture number 1 for a week without heating. Results are in Table (A.10). The treatment gives a measure of the total 'easily mobilised' mercury. No particular chemical species are necessarily extracted, only those which can be dissolved and to which the solution gains access. The results did not yield any important conclusions so the extractions were only performed on some

of the samples with high mercury concentrations.

b. Total Adsorbed Mercury

The procedure is as above but the reaction time is ca. 5 hours. The leaching is carried out on sediments and filtrates which reflect the concentration of mercury in the ambient water. Destruction of some sediments may occur and hence increase the apparent adsorbed mercury. The increase can be accounted for by analysing the component rocks of the sediments, and subtracting the portion of mercury according to the proportion of the rock and its mercury concentration. However the correction was rarely significant due to the relatively low mercury content of the sediment components. The main problem encountered is the presence of sulphide minerals rich in mercury. Cinnabar is not affected by the cold solution, but some attack of iron sulphides does occur. This difficulty only arose in upper parts of the Ngawha Stream, and as can be judged from the cold extractable mercury from iron sulphide containing deposits, little mercury is extracted from the iron sulphide normally (cf. Tables (A.7), (A.10) and (A.13).

c. Total Soluble Mercury

Direct analysis of most filtered waters yields the total mercury concentration. Some waters had to have the mercury adsorbed onto gold and extracted from the gold into 10 ml HNO_3 and 5 ml H_2O (from an original 500 ml sample). In the case of all waters from and near thermal activity care was taken not to lose volatile soluble mercury. Over 99% of the mercury could be volatile (e.g. water from the bore of the Ngawha Springs Hotel site B_1 in Figure (A.5).

The sampling beaker, funnel and flat lid were sunk upright below the water and allowed five minutes to 'equilibriate' as well as being positioned to allow as much water movement as possible. (The lid was separated.) Just before removal, the filter paper was soaked in the water for a minute and the lid slid over the beaker in the pool so that the sediments could begin to settle. After removal the water was filtered as quickly as possible into a freshly opened leached bottle. Both the beaker and the funnel were covered to keep air circulation minimal. The whole process was done as near the water sampling site as possible. Results are in Table (A.11).

d. Organo-Mercurials

The method used was adapted from Westöö (1967 and 1968) who used cysteine acetate/mercuric chloride complexes in a solvent extraction process to separate the organic and inorganic mercury compounds. Several modifications were made

to his procedure to increase the yield from the organomercial extraction. Unlike the original method, the organomercury compounds are analysed by digesting the final extract in digestion mixture 1 (10 ml HNO_3 and 10 ml H_2SO_4 and 5 ml $KMnO_4$ solution) and analysing for mercury by the previously explained cold vapour atomic absorption procedure.

Procedure Alterations

Benzene was purified by shaking with concentrated H_2SO_4, separating and repeating the process. Three times the resultant benzene was treated with a dithizone solution and extracted into an ammonical solution.

Mercury was not detectable in the benzene. Four times solid mercuric chloride was shaken and extracted from purified benzene to remove all detectable mercury extractable into benzene.

The concentration of the cysteine acetate solution was increased from 1% to 1.25%, and the proportion of concentrated hydrochloric acid increased to 5 ml (from ca. 3 ml for 2 to 2.25 gm of sample). The concentrations were increased to make the respective mercury complexes more stable and hence increase the yield of the extractions, and reduce the likelihood of interference by inorganic mercury. (Inorganic mercury is held back as an aqueous chloride complex).

The procedure on page 2279 of Westöö (1968) thus became: 2 - 2.25 gm of sample was homogenised with 15 ml of water, followed by the addition of 5 ml of concentrated hydrochloric acid, 1 ml of 5% purified mercuric chloride and 2 gm sodium chloride. 30 ml of purified benzene was added with shaking and 20 ml separated. The benzene was extracted with 6 ml of the 1.25% cysteine acetate solution, 2.5 ml of the cysteine solution was taken off* and 1.5 ml of 6 N HCl added. Extraction with 5 ml of purified benzene was followed by 4 ml of extract added to 5 ml of cysteine acetate for a final extraction. 4 ml of the cysteine complex was separated then digested as mentioned above.

It was later found that there was no significant contamination caused by using the first cysteine extraction (marked *) instead of the second for analysis. (The extraction of the cysteine acetate extract into benzene was to remove methyl thio groups from methyl mercury. This is mostly done by the addition of mercuric chloride during the original extraction. Thio groups are also removed from the benzene by the washing with sulphuric acid, which also prevents the formation of methyl thio groups from benzene impurities.

Blanks and double blanks were done and gave very similar results by both processes. In fact blank runs consistently gave no detectable mercury from the extraction process, a contrast to all the other procedures, which usually had just detectable mercury present.

e. Elemental Mercury

Sampling for elemental requires more care than for any of the other forms because the element is volatile and can be oxidized. The element can be directly collected by separation from/of other mercury species, or it can be vaporized from a specimen in the field and the loss calculated by analysis of the original total mercury content. The presence of the element in the field can also be checked by spot-tests, atomic absorbtion and surface adsorbtion. Condensates from some hot fumaroles were checked for the possibility of volatile mercury species other than the element, but only traces of an organo-mercurial was found in the organic fraction of condensates.

1. Mercury was collected onto freshly leached gold by passing gas through a tube enclosing the gold. The method was used both in the field and in the laboratory per Figure (5.2). A bubble counter was used to check the flow rate. The gold was

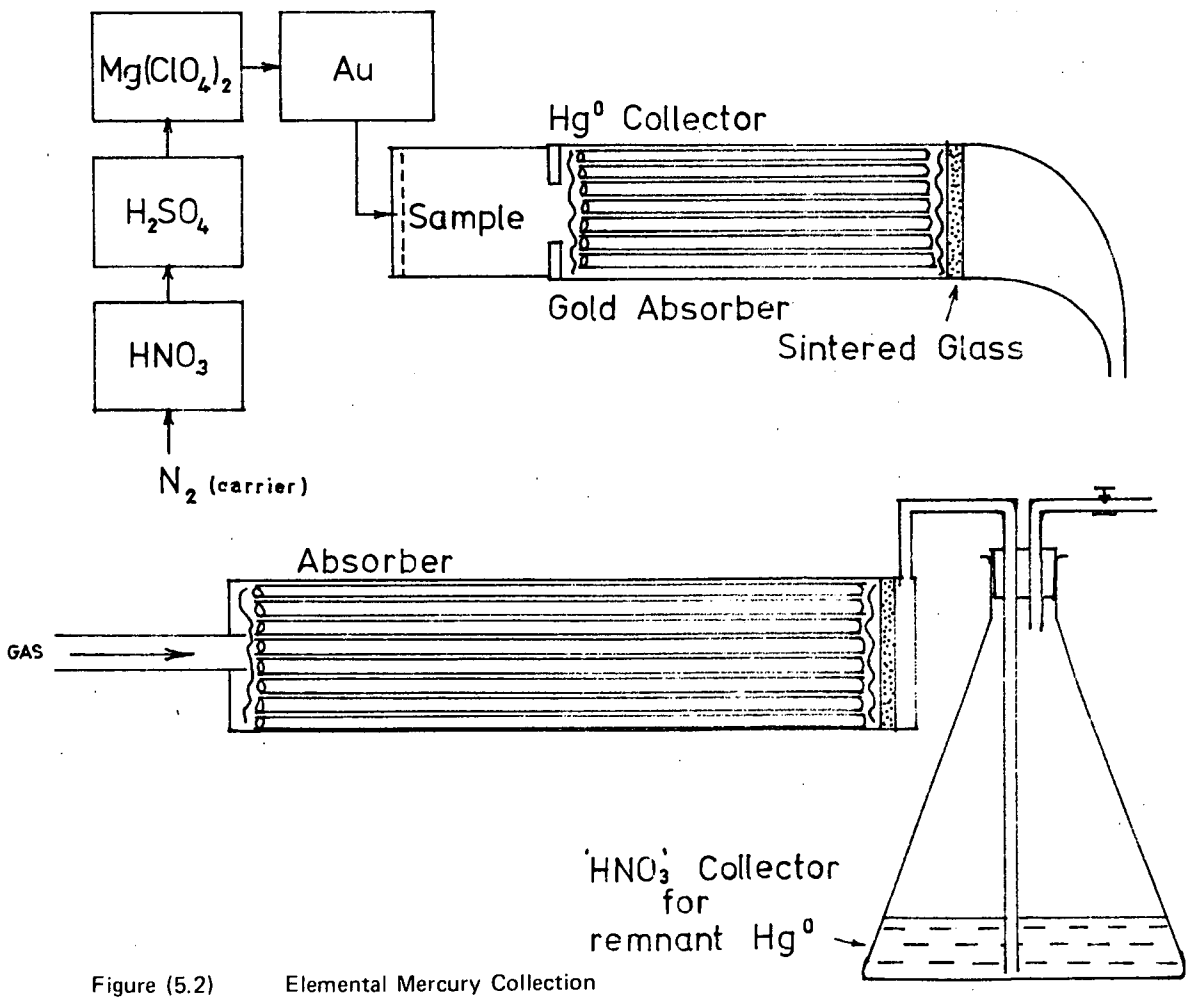


Figure (5.2) Elemental Mercury Collection

rapidly leached using digestion mixture 1, and was ready for re-use at the end of 15 minutes of leaching and a rinse in fresh leaching agent. Solids samples were put into an on-line container and mercury-free nitrogen was passed to carry the mercury onto the gold.

2. Gases were directly passed into a tall container of an oxidising acid leach as mentioned earlier under gas sampling.

3. When collecting liquids it was found easier and more reliable to blow-off the volatile mercury and analyse for the difference due to the small total quantity of mercury present. The element was removed in the field to prevent any adsorbing onto glass or being oxidized by acidification used to keep mercury in solution.

4. Semiquantitative field-testing by use of copper held over gas jets for three seconds commonly showed the presence of mercury by the rapid formation of a mercury film of varying thickness and quality. Results were consistant with quantitative analyses. For the vents with low mercury concentrations and poor gas flow ($\leqslant$ 250 ml/min.) differentiation was impracticable; increasing the exposure time to ca. 20 seconds could cause a useful show of mercury.

5. Paper freshly dipped into a solution of lead acetate (ca. 1.5M) and dilute nitric acid (ca. 1M) was found to develop a film of mercury in the presence of hydrogen sulphide (from the test-gas). The paper is normally used to test for H_2S, however mercury quickly adheres to the surface where the lead sulphide begins to form (dark brown to black). Figure (7.9) shows the effect. The paper can become covered by an extremely lustrous film of mercury where the concentration is high. The test is semi-quantitative and more useful than copper at Ngawha Springs.

To avoid confusion with a possible thick precipitate of lead sulphide it is useful to rub the film on a finger and check that the film is grey and metallic. Drying the paper also reveals a grey sheen if mercury is present.

Testing for mercury in areas with a lower gas : steam ratios commonly made the solution on the paper too dilute (from condensing steam) to be very useful. Tests were done at Wairakei and Karapiti (New Zealand) and at Steamboat Springs, Amedee Springs and Sulphur Banks (United States of America).

(5.5) MERCURY ISOTOPES

A preliminary study was carried out in the Chemistry Department of the University of Tasmania to look at natural variations in mercury isotope abundances (Low, 1974).

Mercury consists of seven stable isotopes : 196, 198, 199, 200, 201, 202 and 204 (Nier, 1950). Only ^{196}Hg has a small natural abundance. The six other isotopes were measured in the work. The greatest mass difference is between 198 and 204 which corresponds to one mass unit in thirty three, or half the difference between ^{32}S and ^{34}S. Hence mercury should show measurable fractionation under suitable circumstances. For instance single distillations of the metal have produced 15 ppm differences in density (Mulliken, 1976).

Samples were digested to form mercuric nitrate, from which ca. 500 μgm was electrodeposited on a small platinum wire (Reimers, Burrows and Krenkel, 1973). The wire was immediately transferred to the heat sample probe of the mass spectrometer and the spectra obtained from the released mercury. 20 to 30 scans over the m/e range 196 to 204 were obtained for each sample (Low, 1974). A standard control of mercury vapour was run with each sample.

The precision of the manual measurement (from strip-chart recorder) was no better than 1%, (0.1% was desirable), therefore variations in isotopic ratios are only significant to the second and third decimal places. Nevertheless some significant differences were obtained (Table (A.14)). One set of data showed a difference equivalent to 8.3 theoretical distillation plates, a difference too large to be due to a lack of precision.

(5.6) CARBON FOURTEEN

Radiocarbon fourteen (and ^{13}C) determinations were made on seven samples sent to the Institute of Nuclear Sciences, Petone, New Zealand (Table (A.22)). All samples were wood and ranged from relatively well preserved to hydrothermally leached and charred. The specmens collected were from large fragments of buried vegetation, commonly whole trees.

The secular correction factors were supplied with the analyses and dates.

Many thanks are due to Dr. A. Rafter for the offer to have the isotope work done, and to Dr. R.C. McGill for running the determinations.

(5.7) THE ELECTRON MICROPROBE

Standard procedures were used such as those described in Zussman (1969). The instrument used was the 'Japanese Electronic Optics Laboratory (J.E.O.L.) model J.X.A. - 50'. Samples were polished under oil and coated with gold. To avoid possible mercury loss, most samples were set in chilled fast-setting 'Araldite', other samples were set in perspex or mounted on a brass base. Several sectioned pipelets were mounted on brass to allow analysis and views both lengthways and across the circular section. Analysed cinnabar from Almaden (Spain) was used as the standard for mercury in cinnabar. Mercury content along a marcasite pipe was found to be constant so a portion was analysed (by atomic absorption) and the remainder remounted as a standard for iron and mercury in marcasite.

A major use of the microprobe was the study of the bacterial production of the pseudomorphs (Figures (8.1) and (8.2) and Table (A.17)). The viewing of 'fine - grained' texture was commonly only possible under the microprobe (used as a microscope) where the grains could also be rapidly identified by X-ray analysis.

(5.8) TEMPERATURES

Measurements were carried out using a -5°C to 150°C and a 0°C to 360°C mercury thermometer. For temperatures in bores the thermometer was put into a brass jacket and heavily lagged to prevent more than 2° loss per minute from 150° in air (12 - 25°C). All measured temperatures were less than 91°C. The thermometer was warmed then lowered into hot bores and left for over one hour and checked for no temperature rise. Gas temperatures were commonly measured by forcing a tube into the orifice of the fumarole and lowering a lagged thermometer as far as possible, 15 minutes was allowed for equilibriation, although 4 - 5 minutes would have sufficed usually.

(5.9) FLUID FLOW

1. Water was determined volumetrically for flows up to ca. 5 l/sec, above this the flow was estimated visually. Just above the confluence into the Ngawha Stream the Te Pukoro Stream had flow measuring facilities set-up (a V-notch dam and scale), hence the large flow was accurately measurable. Table (A.20) and Figures (A.3) to (A.6) give the results.

2. Gas flow was determined by water displacement at one atmosphere pressure. Up to 10 l/min. could be accurately determined, above this flow estimates had to be made. Only two individual vents exceeded 10 l/sec.; one each at the Tiger Bath and Waiparaheke Pond.

For areas with many similar gas vents a few were measured and then the total number counted or estimated to yield the total gas evolution. The flows are given in Figures (A.7) and (A.8) and Table (A.16).

CHAPTER SIX HYDROTHERMAL FLUIDS

A DISCUSSION OF RESULTS

(6.1) THE WATERS

Very little deep geothermal water penetrates close to the surface at Ngawha and the surface 'thermal' water is always diluted to ca. 70% or less. Nevertheless a brief discussion of the various contributing waters is useful. Meteoric surface waters, ground-water and geothermal water are each significant, and are commonly intermixed. All three have characteristics which allow their estimation; in particular, the separation of thermal and non-thermal water. The main discriminants are the O_2, Fe^{2+}, and Cl^- concentration respectively.

(6.2) NON-THERMAL WATERS

These are divided as follows:

i Surface Water a From Outside the Basin
b Basin Catchment Area

ii Ground Water

ia There is very little water entering the basin from without as the basin extends over most of the catchment area for all streams within. However due to the lack of thermal activity in the northern portion of the basin near Highway 12, an area of ca. 1.25 km^2 at the foot of the volcano Waimimiti Ngawha (Figure (3.3)) has been excluded from maps presented in this thesis. The water feeds into the upper tributaries of the Te Pukoro Stream at points 12, 16 & 17 of Table (A.11) and Figure (A.6) as well as by general ground seepage. The net flow from this area is calculated in the next section (ib) as part of the total basin catchment.

Water from the 1.25 km^2 is taken as background for the local non-thermal waters. Mercury ranges from 0.0003 to 0.0005 ppm, and chloride from 2 to 5 ppm. The bedrock of the entire area is basalt which apparently blocks mercury movement (chapter nine) and supplies the high iron content in local ground-water (up to ca. 25 ppm in several places). Limonite is not uncommon where ground-water meets fresh

water. Water temperatures are close to the seasonal ambient; i.e. they range from about 11° in winter to 18° in summer.

ib The basin occupies about 11 km^2 below Highway 12 and ca. 1.25 km^2 to the north. Apart from rain there is no other significant input of non-thermal water. The average rainfall is close to 150 cm per year ('Grasslands', 1975). Hence the total water catchment is ca. 1.8×10^7 m^3 per annum.

Water leaving the basin contains 0.0010 to 0.0013 ppm of mercury (and 3 to 14 ppm of chloride). Neglecting transpiration and evaporation losses and taking into account the background mercury levels, about 16.5 kg of mercury leaves the basin each year in streams. Most of this mercury comes directly from that evolved into fresh waters passing over thermal emissions.

ii The chaos breccia has a very low water permeability (Healy, 1945 and Kear, 1966) and hence restricts downward and lateral movement. Therefore all ground-water eventually ends up in the streams and has its origin as local rain. Because there are only two streams which drain the basin, virtually all ground-water leaving the basin must do so via these streams.

Ground-water moving through basalt flows may contain considerable concentrations of iron, up to 25 ppm. This is the major useful characteristic of the ground-water. The pH of ground-water appears to be more narrowly confined than that from other origins. Probably this is caused by the lack of (oxidizable) sulphide and the buffering from the surroundings. Wherever water rich in iron was found, the pH was inevitably very close to seven. The mercury content of 'pure' ground-water was about 0.00005 to 0.0001, for example the strong seepage just to the north-east of the waterfall at N15/377351.

(6.3) THERMAL WATERS

Evidence supports only one deep source for all the geothermal waters: all hot pool compositions parallel those found in the deep bore NG1 (Ellis & Mahon, 1966; Ellis, 1970; Giggenbach and Lyon, 1977). Hydrogen and oxygen isotope ratio studies show that all waters, whether surface or sub-surface, are derived from meteoric water and have no suggestion of water from a juvenile origin (McDonald, 1966; Lyon, 1977). A dominant characteristic is the high boron content and the ratio of chloride to

boron (as HBO_2) which lies between 0.42 and 0.45. Elemental mercury concentrations were found to be very high, and tended to parallel chloride in unexposed waters. However the chloride content is more reliable for determining the geothermal component because it is not volatile.

a. Flow

'Thermal' water provides only a small fraction of the total water output of the basin. The directly measured total water flow (mostly stream waters) from all thermally active sites is about 2250 ml/sec (Figure (A.3) and Table (A.20)). A more reasonable figure for the geothermal flow is arrived at by comparison of the chloride content of mixed waters with those of waters of 'entirely' (deep) geothermal origin. The most appropriate water appears to be that from the bore sampled by Giggenbach and Lyon in mid 1977 (Lyon, 1977). The water contained 707 ppm of chloride.

By mass-balance of the chloride in the 46 to 47 l/sec total basin outflow per Table (A.20) the geothermal input lies between 0.56 and 0.74 l/sec, and is about 0.6 l/sec overall. (Comparison with the much deeper bore NG1 yields a flow of only 0.45 l/sec after correction to surface temperatures and pressures).

b. Temperatures

These have been partially discussed in chapter three, and the data are in Tables (A.12), (A.16), (A.20) and (A.21). Ambient air temperatures affect the pool temperatures to some degree. The surface temperature is most variably affected in hot waters, but by a few centimetres into the muds there is little change. The movement of non-thermal water due to weather changes is also important: e.g. the Tiger Bath cooled 20°C during a week of heavy rain in 1973. Most pools lie in surface-water dominated ground and are heated by rising gas, and are thus subject to considerable changes, including Eh and pH.

Apart from the considerable short-term temperature changes possible, (up to 45°C measured) there appears to be no trend in temperatures during historical time. The highest near-surface temperature measured in recent times is 92° in 1976 (Barnes, 1977), and the oldest recorded highest temperature was 99° from a bore 30 m deeper about 80 years ago (Griffiths, 1898). The latter is the highest recorded near-surface temperature. Figure (3.8) shows the recorded surface temperatures as found at ca. 5 cm depth in winter 1973, when the highest recorded temperature was 90° for a small area south-east of the Tiger Bath at about 1 m depth (in 1976 the temperature had dropped below 60°).

c. pH

The thermal solutions range from just alkaline of neutral (pH 7.5 at 65°) to distinctly acid (pH 4 at $\leq$ 40°C). The majority of pH's lie between 6 and 3 units. The field results are given in Table (A.20). Strong acidity is due to bisulphate in quantities up to 5,000 ppm formed from the oxidation of sulphides. The most acid environments are the cool ebullient pools with a substantial fresh water component from either seepage or direct inflow. The hottest and least diluted waters have the highest pH's; these are commonly between 5.5 and 6.8 units for surface and near surface waters.

During the mid to late winter of 1973 the pH's were generally one to two units lower than those of late summer 1976. This is probably due to the lower rainfall and greater evaporation which occurred in the summer. Consequently less oxidizing water enters the thermal areas. Deep waters from bores and a few very hot baths were little changed in pH.

pH may vary from week to week or less by as much as 0.75 units. The variation relates mostly to streams and pools with appreciable dissolved sulphide or H_2S evolution. Other influential factors are the dissolved gas content (buffering), evaporation (total salt concentration), the proportion of aerated to non-aerated water, and the residence time of the water(s) in the body. Some of these factors depend on further parameters, such as weather and the relative flux of gas to the various aqueous components and their solutes.

In the cinnabar depositing areas pH commonly lies between 5 and 2.5. Whereas the pyrite/marcasite conditions range from 7.5 to about 3.5. Pyrite is favoured by pH's of 6 and above.

d. Buffering

It was noticed that many of the 'thermal' waters changed pH rapidly just after separation from the field occurrence. The changes were not due to oxidation because they are too fast and there was no change in dissolved sulphate. Below is a list of some of the changes observed. The major buffers present are boric acid and bicarbonate, these are present in concentrations up to several thousand parts per million. The considerable CO_2 in the co-existing gas phases enhances buffering, particularly where dissolved bicarbonate or carbonate are formed in significant quantities. Minor buffers in near surface conditions are ammonia and silica but they only rarely exceed 100 ppm each. Bisulphide is so low that any influence on pH is insignificant.

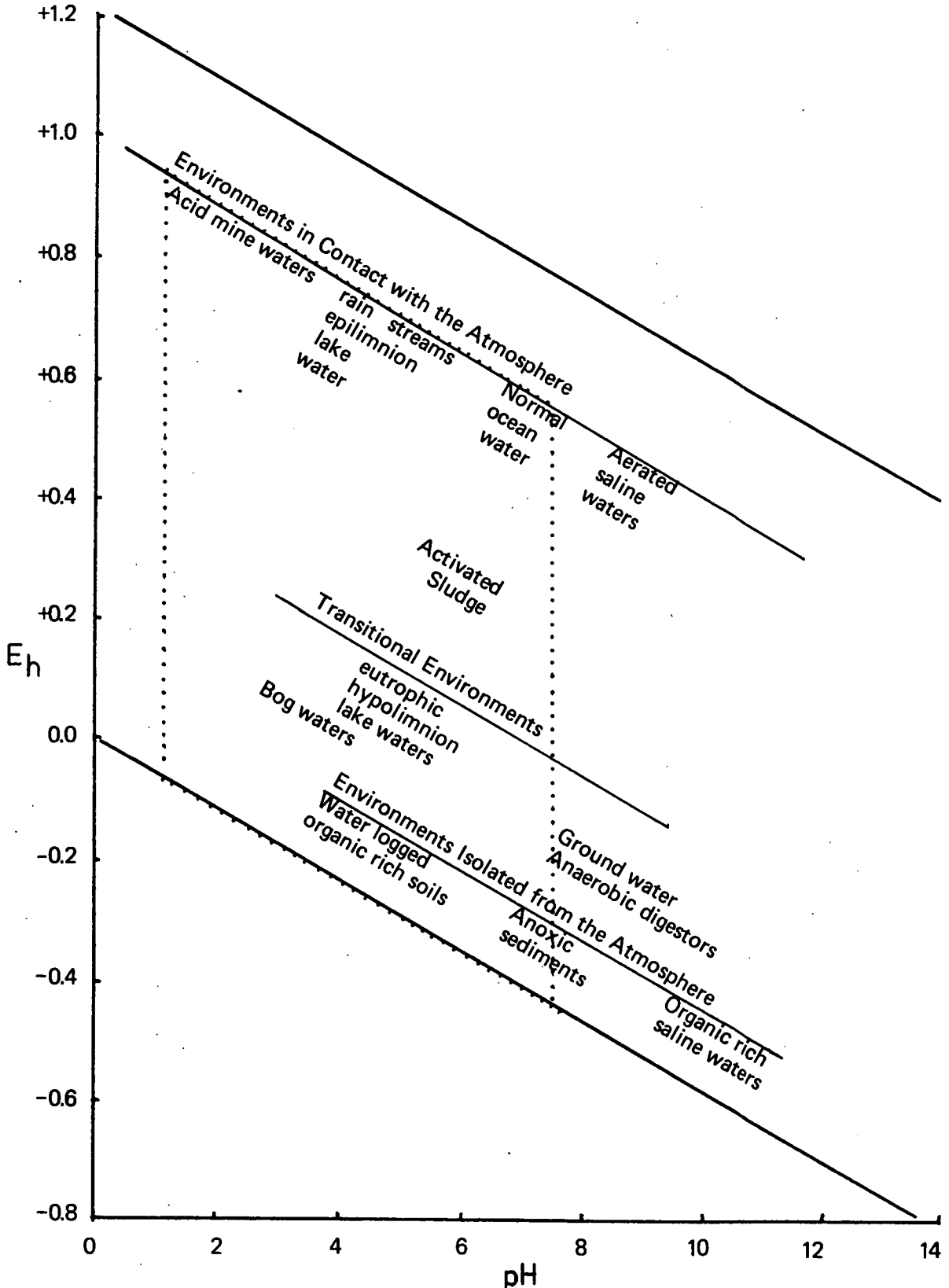


Figure (6.1) Relative positions of various environments as characterized by E_h and pH. The dotted lines contain the near surface environments at Ngawha Springs.

TABLE (6.1) pH Changes Caused by Degassing

Location		pH in situ	pH on standing
Waima, gaseous section of stream,	19°	5.0 - 5.4	1.9 - 2.2
Jubilee, hottest thermal bath,	49°	6.2 - 6.3	7.4
Tiger, most ebullient bath,	41°	5.3 - 5.6	3.8
Bore, 120 m below 'Ngawha Springs Hotel'	52°	6.2	6.9
Tuwhakino Stream, Domain at a time of relative drought	18.5°	ca. 4.25	ca. 2.5

Where buffering was noticed it appeared to be due to a volatile species which most commonly buffered between pH's of 6 and 7. Hence the pK_a of the buffer lies between 6 and 7. The above table shows the general trend of hot pools (which usually have the highest pH's) are buffered to between 6 and 6.5 units, and cool baths (which have the lowest pH's) are buffered to between about 5.4 and 6 units. For many of the cool pools the capacity of the buffer(s) is exceeded.

Boric acid has a pK_{a_1} = 9.2 (at 20°; Weast, 1976) and so is not close enough to any of the observed pH's to have any significant effect, nor is it volatile. For H_2CO_3 the pK_{a_1} = 6.4 (at 20°; ibid). This pK_a is close to optimum for the observed pH range of buffering, and is in agreement with the observation that the buffer is volatile, and more so in acid solutions.

Silica probably buffers deep waters where the temperature is above ca. 175° and solutions are silica-saturated.

e. Eh

Waters range from air-saturated and acidic to anoxic, organic-rich and weakly saline sludges containing sulphate reducing bacteria. Such conditions cover an Eh range of ca. +0.95 to -0.4 volts, respectively. Figure (6.1) indicates the variety of conditions occurring at Ngawha Springs. As a thermodynamic system the superficial thermal area is open: commonly oxidizing and reducing conditions are in very close proximity and may intermix.

The mixing of aerated water and geothermal water or gas causes the Eh of a thermal discharge to change rapidly. The change is not necessarily uniform, and relatively oxidizing and reducing conditions may be present within the one small water body.

Eh and pH were found to be inter-related in many sulphurous waters. As pH fell due to bisulphate formation in oxidizing waters, the Eh rose. This is caused by the

simultaneous increase in oxygen and acidity, and was observed to cause cinnabar formation in the field. The effect is explained by the equation:

$$2H_2O \rightleftharpoons O_2\,(g) + 4H^+ + 4e^- \qquad E^o = 1.229\,v$$

i.e. $Eh = 1.229 + 0.015 \log f_{O_2} - 0.059\,pH$ at 25°

Under the most oxidizing conditions found (near saturation with air and pH = 1.25) Eh was +0.95 v. The usual Eh range for streams is about +0.65 to +0.4 volts. The coexistence of pyrite/marcasite, sulphur and bisulphate in many thermally active parts of the Tuwhakino Stream suggests Eh's below -0.66 v. occur in some 'fresh' water sediments (calculated from data in chapter 7 of Barnes, 1967).

Cinnabar appears to form only in areas where Eh exceeds +0.2 volts and the iron sulphides favour conditions below ca. +0.15 volts.

The Eh of the 'pure' geothermal fluid is not yet accurately calculable because there is insufficient data on mineral pair assemblages, relevant chemical species or isotopes. However a minimum fluid Eh can be calculated. The logs of the 591 m drill-hole (NG1) show that at "1406 to 1412 feet" there is crystalline pyrrhotite in grey siliceous rock and other 'iron sulphides' present below this. (Healy, Skinner and Bowen, 1966). These are probably near equilibrium with the surrounding hot fluid, ca. 210° C, since the residence time of the fluid in the system has been estimated to be at least 0.2 years (Robinson, 1977), and there is no direct escape for the fluid in the vicinity of the bore. Assuming fluid equilibrium with the pyrrhotite, then because at shallower depths pyrite occurs, the equilibrium boundary where both sulphides coexist is encountered by rising fluids. The pH in NG1 is about 7.4 (Ellis, 1970) thus from the data in Barnes (1967) the equivalent Eh at near surface temperatures and pressures is about -0.48 volts, or log $aO_2 = -87$. (This may explain the presence of hydrogen in the gases.) Thermal waters which have undergone some degree of mixing yet still contain about 50% of the original sulphide unoxidized have an Eh of about -0.28 v. Hence the Eh of the thermal water before mixing probably lies between -0.28 and -0.48 volts. The larger negative potential characterises water similar to that of NG1 which has had little contact with other waters.

(6.4) COMPONENTS OF THERMAL WATERS

Mixing of the geothermal water with surface waters and evaporation causes the total dissolved salt content to range from near background levels to about 8,000 ppm (0.8%). The main components are borate, chloride, bicarbonate, sodium, total

sulphate, silica, ammonia and potassium (Ellis and Mahon, 1966). Important minor species are total sulphide and mercury; iron is less than 0.1 ppm in geothermal water and is only important in some ground waters. Changes in the chemistry of the solutions also occur due to the escape of volatile components. Analyses of waters are included in Table (2.1).

As the geothermal water rises some dilution occurs and chloride analyses indicate that by comparison to NG1 they are about 50% diluted when they near the surface. The boron, chloride and mercury concentrations all strongly relate to the (deep) 'thermal' content of most waters. The mercury concentration correlates closely with temperature and chloride content of the superficial warm to hot waters in deep pools. Once water leaves the proximity of its superficial source, the mercury content has a rapid loss of correlation with the 'thermal' content (Tables (A.11) and (A.20)).

a. Chloride

The range is from a background of 2 - 3 ppm in streams to 1625 ppm in NG1. Comparison of the bore-waters of NG1 and the one found by Lyons and Giggenbach in 1977 (which has the highest near-surface chloride content) indicates a minimum dilution ratio of 1.77 for surface 'thermal' waters before evaporation, (after correction for steam condensation from the deeper fluid). In spite of considerable dilution there is a characteristic ratio of Cl^- to HBO_2 for all warm waters in the basin: the ratio is ca. 0.42 to 0.45 (Ellis and Mahon, 1966). A simple relationship between mercury and chloride concentrations is not possible in mixed or evaporated waters because mercury may react and precipitate, become adsorbed or volatilize. In the deepest least-mixed waters, the mercury to chlorine ratio is about 10^{-3} to 10^{-4}. However the separation of the gas phase effects the mercury in solution.

b. Sulphur

The total soluble sulphide content of the deepest waters (NG1) is 4 ppm (Wilson, 1966), for surface springs the range is 1 - 10 ppm (Ellis and Mahon, 1966). Most warm waters contain a total sulphide concentration of between 2 and 7 ppm, and have pH's in the range 6.5 to 4 units, hence the reduced sulphur species H_2S dominates with subordinate HS^- in the near neutral range, $[HS^-] \leqslant 3$ ppm or 10^{-4} M.

Sulphate is usually abundant in surface and spring waters (100 to 2500 ppm), but much lower in bore-waters, ca. 15 to 100 ppm (Ellis and Mahon, 1966). Surface waters are higher in sulphate (and hence more acid) due to the oxidation of aqueous and gaseous H_2S.

c. Iron

Very little iron is present in the geothermal fluids, up to 0.1 ppm has been detected in bore fluids. Ground-waters passing basalt contain appreciably more iron; 2 - 25 ppm. On standing in air many ground waters deposit limonite, including the water at 50°C in the bore sank 107 m into basalt below the Ngawha Springs Hotel, and ca. 45 m from emissions in the upper Tuwhakino area.

d. Other Metals

Although minor antimony and arsenic concentrations occur in very recent sediments of the upper Tuwhakino area (up to 2.1% Sb and one occurrence of arsenic-rich mud) neither metal was detected in water. However 0.2 ppm As was detected in the Jubilee Bath in 1944 (Fleming, 1945). Copper was able to be plated from the Tiger Bath in 1973 (Figure (7.10)) but not in 1976, however dissolved (not suspended) copper was undetectable (< 0.1 ppm) but was just detectable in bore-water from the 107 m bore at the Ngawha Springs Hotel.

(6.5) MERCURY IN WATERS

Total dissolved mercury ranges from just below 0.001 ppm in mixed waters to 0.35 ppm. In addition many ebullient surface waters/pools contain mercury adsorbed onto colloids in concentrations yielding up to 3.4 ppm for the in situ water (Table A.11) and hot bore-waters (down to 110 m) have concentrations between 0.04 and 0.11 ppm total mercury. Gas leaking from NG1 contained at least 3 ppm (μg/l) of mercury which infers the deep geothermal fluid has a minimum concentration of 0.5 ppm Hg.

The highest dissolved mercury concentrations occur in the hottest waters and the most ebullient small pools (even if cool). Cool to warm pools show a closer correlation between mercury content and gas evolution, especially where the gases are obviously sulphurous. The highest total mercury contents are in pools which have the most sulphurous colloidal suspensions in turbid ebullient water. Mathematical formulation of the correlations is unwarranted due to the scatter of the data and a lack of controls. For example the volatility of the mercury in the natural solutions causes too much dependence on physical parameters which relate to the ease of access/escape of mercury into the air.

The only soluble mercury species found was the element. Nearly all small bodies of non-flowing water (and the percolating gas) are close to saturated with the element. Consequently mercury is readily lost from the near-surface waters, and may fall below 0.001 ppm unless gas percolation is present: e.g. the exposure of fresh hot bore-water bore with 0.06 ppm total mercury (all dissolved) left only 0.0007 ppm Hg in solution after ca. one minute.

The adsorbed mercury species also appear to be dominated by the element, since mercury is easily 'breathed' off the colloidal filtrates into mercury-depleted solutions. More convincingly, during periods of acid-oxidizing conditions in the presence of percolating H_2S (e.g. fresh stream-water moving into an acid pool), cinnabar forms from the adsorbed mercury and yields red coatings on the substrate. This was also demonstrated in the laboratory on natural and synthetic materials, where oxidation was found to be necessary for the observed process to proceed.

All waters containing less than 0.005 ppm total mercury appeared to contain significant 'non-volatile' mercury. It is uncertain as to whether this is partly due to the presence of elemental mercury in air, soluble species, very fine colloidal dispersion(s) of insoluble mercury compound(s) or some other cause. Natural waters leaving the valley contained about 0.001 ppm of mercury, of which 40 - 70% was non-volatile. The oxidizing nature of the streams outside the thermal zones makes it probable that some mercury compounds are present.

In summary less than 0.0005 ppm of mercury in any solutions can be attributed to dissolved mercury compounds. Geothermal solutions contain far less than 0.0005 ppm non-volatile dissolved mercury, and contain at least 0.1 ppm total dissolved mercury (as the element) before mixing with surface waters.

(6.6) GAS

Gas is the main thermal fluid evolved from the Ngawha Basin. It is present in all thermal discharges, and may compose the whole of a few small discharges. The average compositions of the gases are shown in Table (6.2). Components vary by a few percent, but emanations are of similar composition throughout the valley. Rarely H_2S concentrations are undetectable due to dissolution in surface-water. Total measured gas-flow for the basin is about 1300 l/min (21.5 l/sec) at one atmosphere pressure.

The deep thermal gas is of very similar composition (cf. Ellis, 1970 and Giggenbach and Lyon, 1977) and is slightly higher in H_2S and NH_3 and lower in hydrocarbon concentrations than surface emanations. The bulk of the gas is composed of carbon dioxide and methane (97 - 98%). The fluid from NG1 at a pressure of one atmosphere (and 228°C) is ca. 14% gas, 21% steam and 65% water by weight. This contrasts the overall surface emissions which are 93.5 to 97% gas and ca. 2.5% water by volume, the remainder is water vapour. The wet gas to water ratio is about 40:1 (v/v). Consequently, the Ngawha fluids are very gaseous by world comparison, even though

Table (6.2) Average Gas Composition - all zones; %

(mostly after Ellis and Mahon, 1966).

CO_2	90
CH_4	7
(H_2O	saturation level)
N_2	2
H_2	0.8
H_2S	0.02
NH_3	< 0.0075
Hg	< 0.05

This data is for 'spring' gases, temperature < 60^{o}.

they constitute only about 7% of the total fluid by weight. The fall in the percentage of gas in the total geothermal fluid which reaches the surface implies that the deep (ca. 600 m) geothermal fluid is diluted to less than 50% during the ascent to the surface.

Tables (A.12) and (A.16) and Figures (A.7) and (A.8) give mercury analyses, temperatures and flow rates for the surface gases. The total fumarolic gas flow of 1300 l/min may not include the total gas loss, for some gas may escape by diffusion processes and dynamic exsolution from deeper pools percolated by gas.

Temperatures of the subterranean gas are the same as the accompanying geothermal fluids until the 'water-table' is reached where direct and rapid mixing with the surface waters occurs. In and above the water-table are the pools and thermal baths which are commonly cooler than the gas percolating through them. The temperature differences are rarely more than 20°C, but in the few 'very hot' baths (≥ 45°C) the difference occasionally reaches 35°C.

It is gas ebullience which causes most of the sapping and erosion of stream and pool beds and banks by removal of silt and smaller grains. The ebullition makes water turbid with fine grained materials which may drift off in the currents. Pools with vigorous gas activity have deep throated orifices per Figure (6.2), about which only

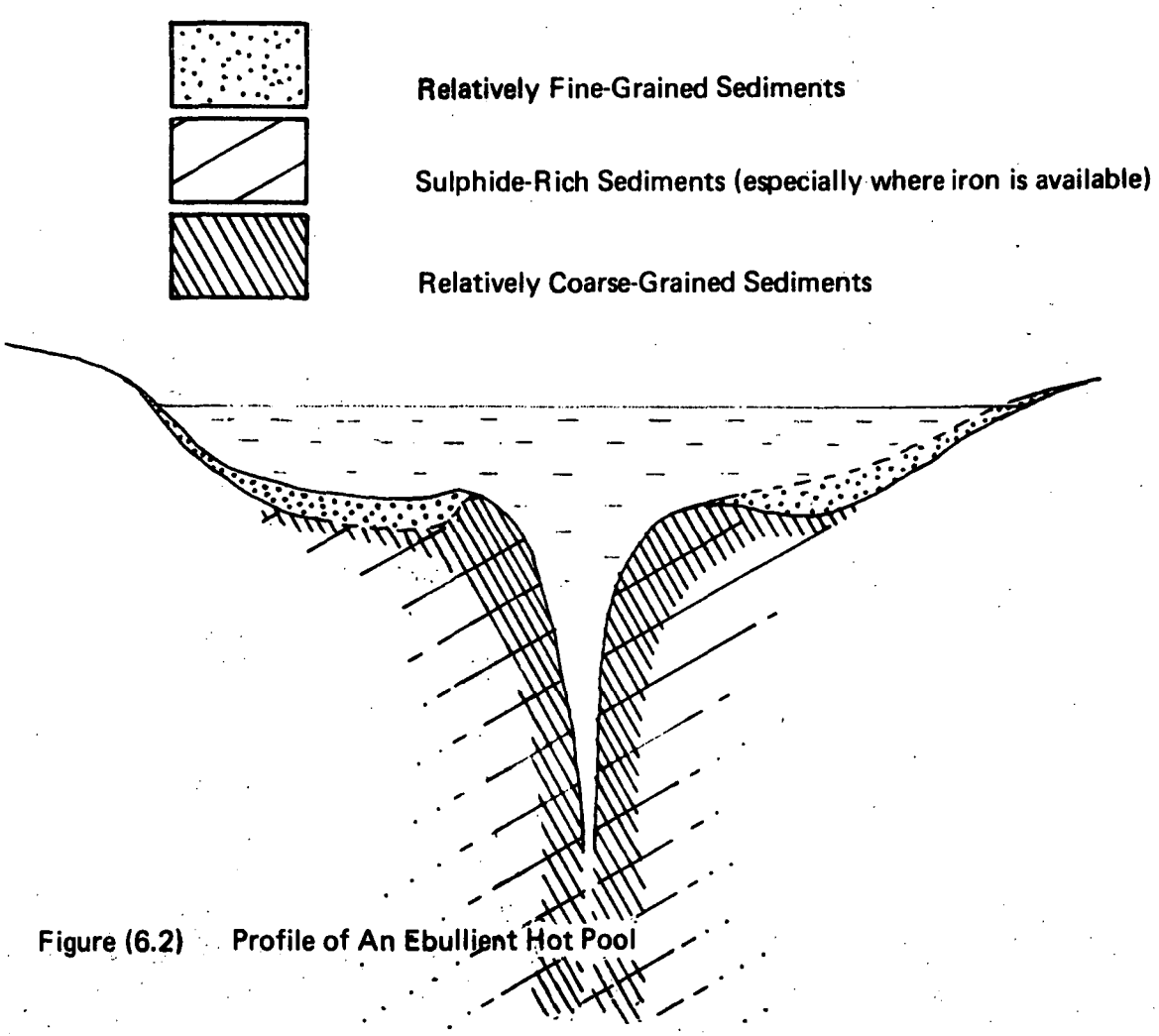


Figure (6.2) Profile of An Ebullient Hot Pool

coarse grains can remain and settle. Further away from the fumarole vent the finer grained clasts settle. In the hot ebullient pools (e.g. Tiger Bath) the most sulphide-rich material forms in the coarser sediments and in the walls of the vents. Near basalt the walls of gas vents in the less vigorous hot pools (100 - 250 ml gas/min and temperature $\geqslant$ ca. 28° C) are commonly marcasite. Pools with no vigorous gas activity usually have an equitable distribution of matter and no significant depressions about the gas outlets.

Pressures in the surface environment rarely exceed the hydrostatic load. In the 590 m bore (NG1) the closed-in pressure developed was ca. 56 atmospheres (Banwell, 1965) very close to the hydrostatic load. Only in a few rare instances have pressures of 2 to 3 atmospheres above hydrostatic load been encountered, and they have all dropped back to normal within hours of being discovered (e.g. Davey and van Moort, 1974; Griffiths, 1898).

a. Sulphur

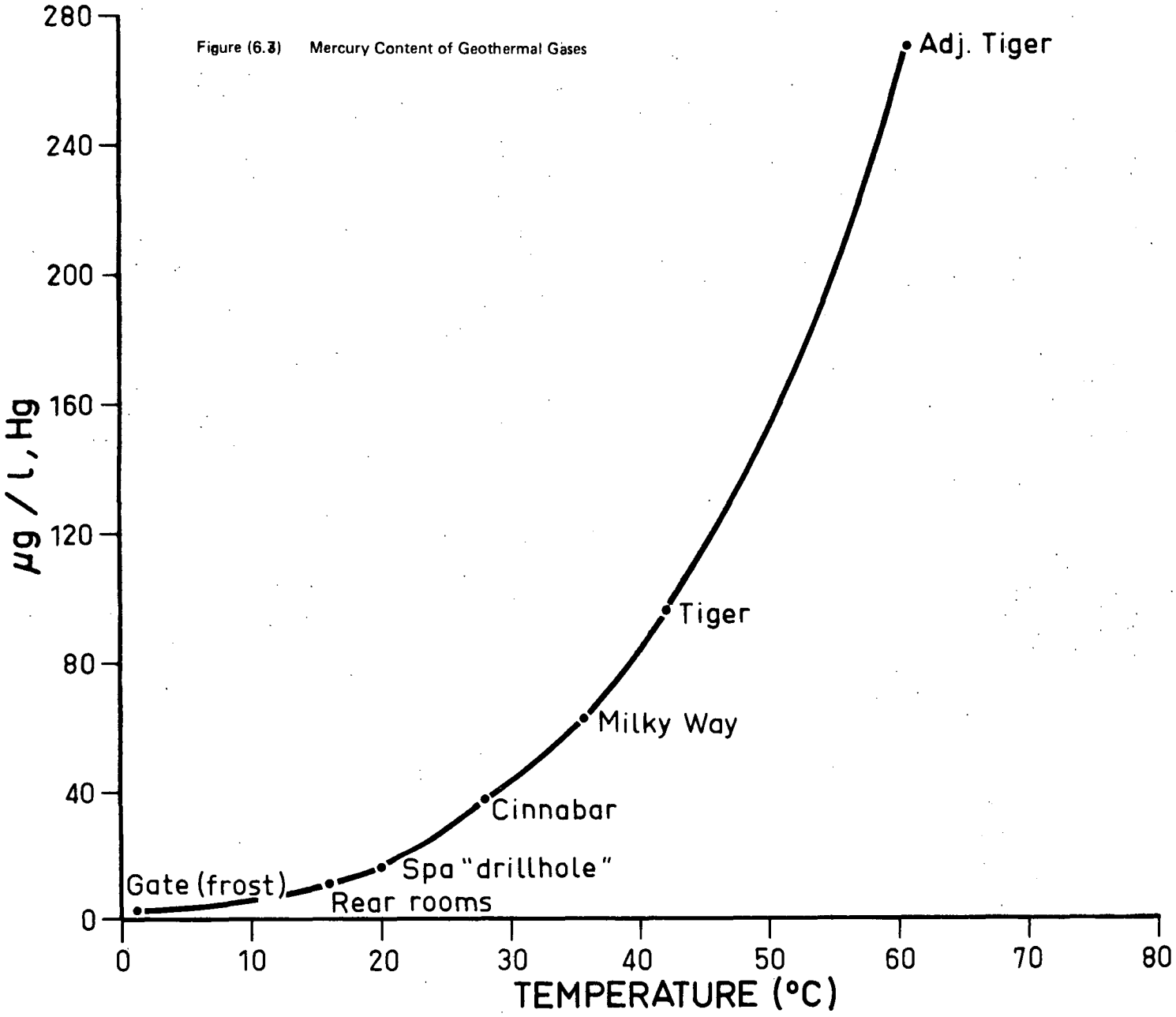
Hydrogen sulphide accompanies almost all surface emanations in quantities ranging from 0.1 to 400 ppm, and is present in the deep drill-hole gas to the extent of 0.7 mole % or ca. 6,000 ppm (Ellis, 1970; Wilson, 1966). Other sulphur gases have not been detected. The lowest sulphur contents are associated with gas percolating into the fresh waters, where dissolution into water below the fumarole mouth is probably responsible for the loss of H_2S. Where considerable flow of gas percolates into relatively fresh waters, the sediments are commonly very sulphurous, some contain over 90% elemental sulphur (Rabone, 1972). Isotope analyses are compatable with a basaltic to andesitic magma source for the H_2S, which has $\delta^{34}S$ values of +2 to +3‰ (Giggenbach and Lyon, 1977).

The ^{34}S contents of $SO_4^{=}$ and H_2S are very similar and do not allow meaningful temperatures to be estimated from any of the near surface bores and springs. Samples of HS^- and $SO_4^{=}$ from NG1 have a difference of 21‰ (Wilson, 1966) which corresponds to an equilibriation temperature of ca. 300° C (Robinson, 1973). Sulphur isotope studies were not done on any minerals because the low temperatures, the presence of sulphate reducing bacteria and the variably open system conditions make any results useless for quantitative evaluation.

(6.7) MERCURY IN GASES

Mercury may collect on many materials in the Ngawha Springs area not even close to springs indicating air-borne mercury in significant anomalous concentrations.

Figure (6.3) Mercury Content of Geothermal Gases



Analyses for mercury in the thermal gases showed that most were saturated with elemental mercury (Figure (6.3) and Tables (A.12) and (A.16)). In most gases no other form of mercury was detectable, however traces of an organomercurial were detected in condensates from the Tiger Bath area. Maximum mercury concentrations found were 750 - 790 μg/l or 3.9 μM/l, which in the hottest ebullient gases (ca. 85 to 90°C) is undersaturation by 10° to 15°C.

The presence of mercury-saturated water in the bores which reach below the cinnabar deposits to over 100 m depth (Table (A.20) indicates that the mercury is not from thermal decomposition of local cinnabar. The minimum of 3 ppm (Hg^o) in the gas of NG1 supports a deep origin for the element, (samples of the hot fluid could not be obtained).

The highest mercury concentration obtained corresponds to saturation temperatures of ca. 75°C. Therefore below 75°C mercury must condense from the gas phase of undiluted geothermal fluids. Since the mercury concentration increases exponentially with temperature (Figure (6.4)), the greatest rate of mercury condensation with falling temperature occurs at the highest temperature of saturation. The linear thermal gradient thus implies that the maximum deposition of elemental mercury per unit volume of ground is also near 75°C. This corresponds to maximum depths between 170 and 80 m below the surface of the basin at which the condensation of mercury can begin for the thermal gradients which are between 350° and 625°C/km respectively. As expected condensed (liquid) mercury is very common near warm to hot springs (Figure (7.11) and Table (A.10)). Consequently elemental mercury is widely spread and the vapour is detectable in much of the basin including soil-gases, swamp-gases and air.

The presence of liquid mercury is also influenced by diffusion which is discussed later. Diffusion causes a decrease in the amount (or the concentration) of mercury expected in a given locality by allowing the escape of mercury through permeable rock. This is strongly supported by the anomalous halos of elemental mercury in the Ngawha Basin (Figure (9.2)). Surface waters also dissolve elemental mercury and reduce the amount of observable liquid.

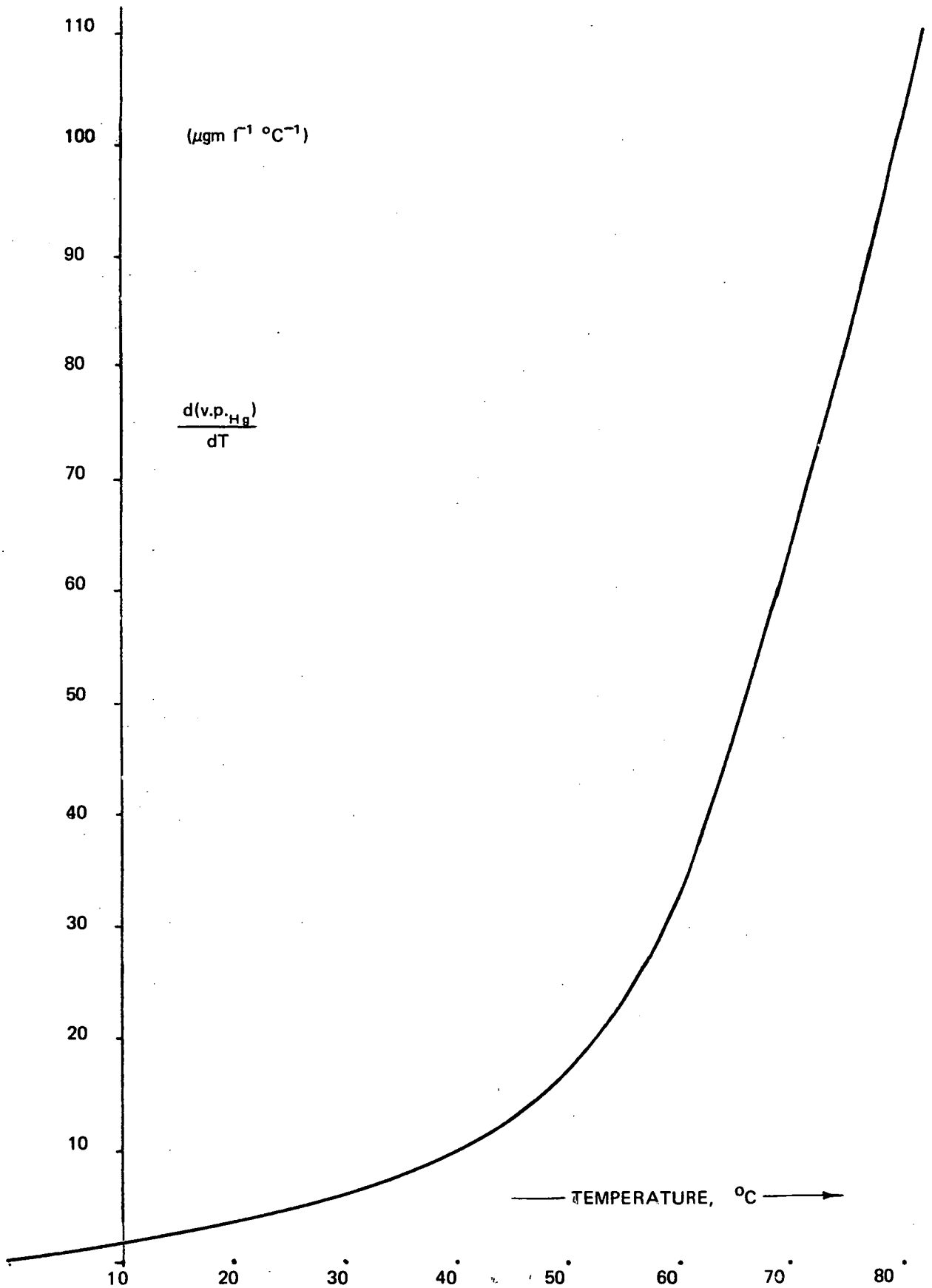


Figure (6.4) The Rate Of Change Of Mercury Vapour Pressure With Temperature

The diagram shows how the vapour pressure of mercury changes with temperature. Note the dew-point concentration rapidly increases with rising temperature above about 20°C, hence the precipitation of mercury from gases above 20°C upon cooling is very efficient.

CHAPTER SEVEN HYDROTHERMAL MINERALS

In common with the majority of other mercury deposits the mineralogy at Ngawha Springs is simple. The main minerals present are native sulphur, pyrite, cinnabar, marcasite, native mercury and haematite. Very minor minerals are sulphides of antimony and arsenic, ammaugnite and metacinnabar (pyrrhotite has been found below 427 m (Skinner, 1966)). Silica sinters are uncommon, the only known occurrences are at Waitotera Pond, the Tiger Bath and the Domain, and another is south-east of Lake Omapere at N15/334408. All of the above minerals except for pyrrhotite occur in the uppermost 10 m of the thermal zones, only pyrite and native mercury may also penetrate deeper. No copper minerals were found although it is present in some sulphides and plated an iron spade (Figure (7.10).

(7.1) IRON

Of nine iron minerals found (related to thermal activity) five have primary occurrences. They are marcasite, haematite, limonite, pyrite and goethite. The first three minerals occur in the richest parts of the cinnabar deposits which are present in the uppermost three metres of the ground. The latter two minerals are rarely seen with cinnabar, although pyrite may be common in the low grade cinnabar below the uppermost three metres. The iron sulphides are the most common iron minerals in the cinnabar deposits, with haematite common in some cinnabar-rich horizons. Whilst in the field area marcasite, limonite and haematite were observed to form; the iron sulphide was commonly precipitated as FeS and gradually changed to FeS_2 (analyses in Table (A.4).

The secondary minerals are mainly hydroxyl sulphates, hydroxides and sulphates. The minerals determined were coquimbite, melanterite, jarosites, pickeringite and limonite.

As discussed earlier iron is transported by ground-water; the main source of iron is the basalt, not the geothermal fluids. Basalt below the Tuwhakino area and adjacent to rising thermal fluids is very pyritic (Jones, 1939). However it was only marcasite which was observed to be directly related to geothermal cinnabar deposition, apart from included clasts neither iron sulphide contains any other mineral phase.

(7.2) MARCASITE

The mineral occurs throughout the active parts of the southern side of the

B

A

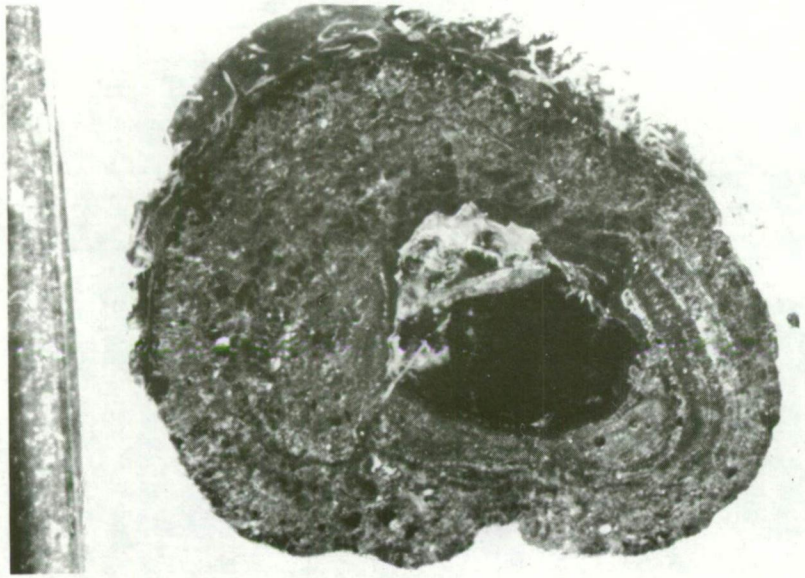


Figure (7.1)

a: Cross-section of a marcasite pipelet. The tubes form from the reaction of Fe II in ground-water with H_2S in gas percolating through the water: the marcasite thus formed encases the gas vent and displays series of semi-annular patterns. Magnification 18x.

b: Haematite pipelets formed from the oxidation of marcasite, 1/7x. Note the branches on some pipes to the upper left of centre.

c: Marcasite from the Tiger Bath area, 1.6x. Left: a partially pseudomorphed root. Centre: a nodule formed in superficial warm sulphurous sediments. Right: a ruptured pipelet; probably due to an obstruction to the gas flow.

d: A large ragged nodule from the Tiger Bath. It has thin patchy cinnabar irregularly distributed over the outside surface. 2/5x. 30 x 18 x 11 cm^3 .

C

D

Iron Minerals.

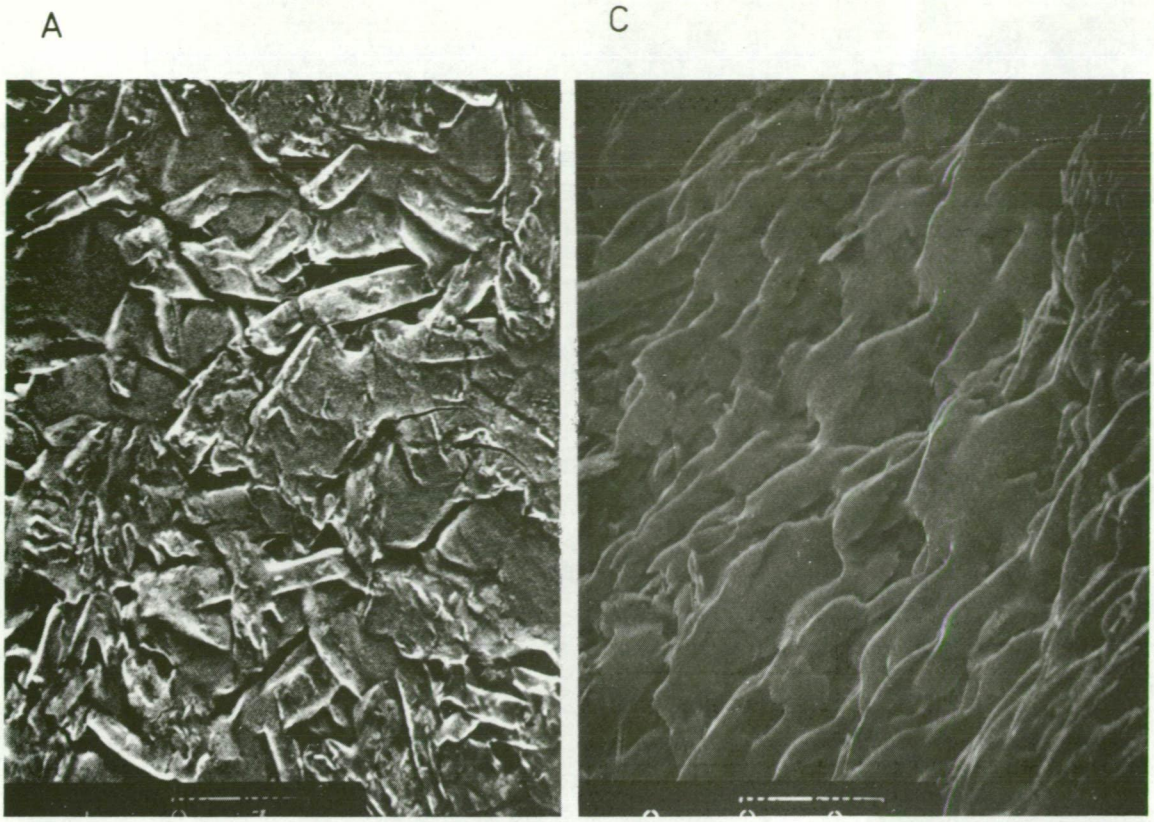
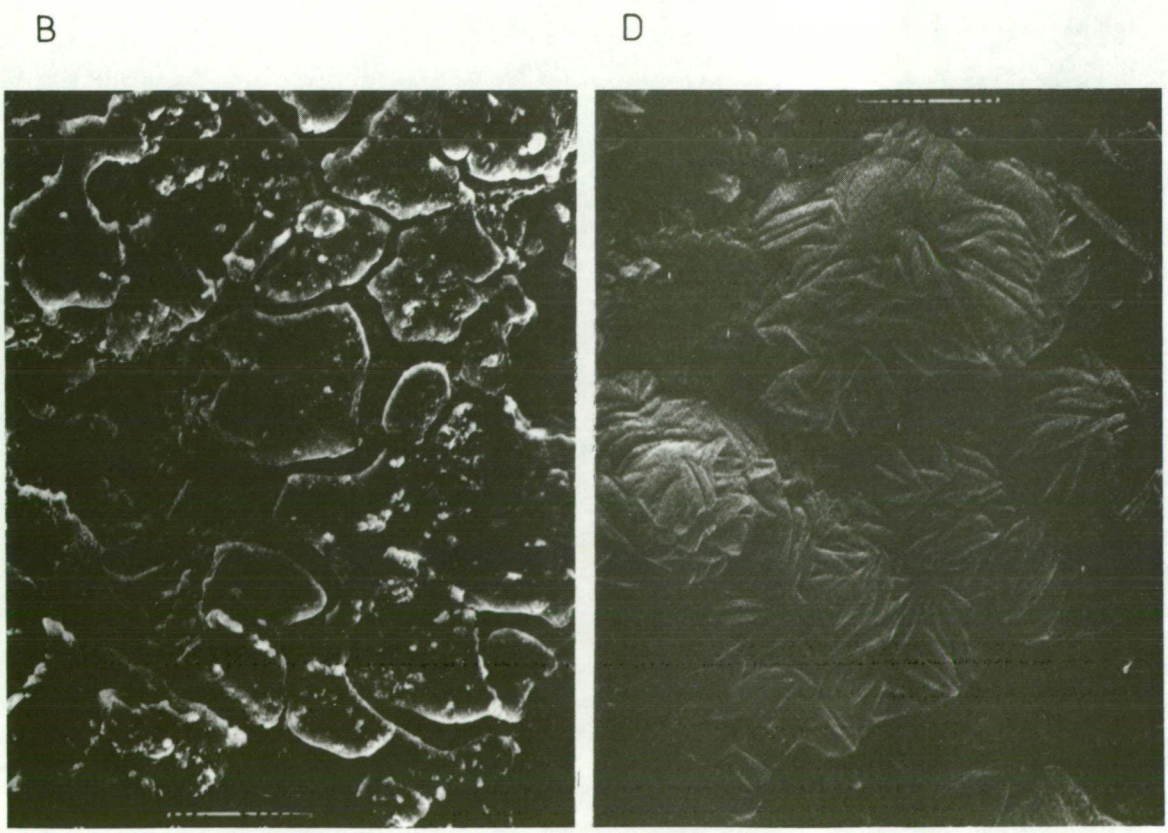


Figure (7.2) A: Semi-tabular marcasite grains in a pipelet; 3500x.
B: Desiccation cracks in a small fresh pipelet; 10000x.
C: Overlapping grains of marcasite on the external surface of a pipelet. An oblique view, 3000x. Commonly minor cinnabar may also be present on this surface as a thin 'amorhpous' coating.
D: Rare marcasite rosettes near the centre of one side of a pipelet annulus.



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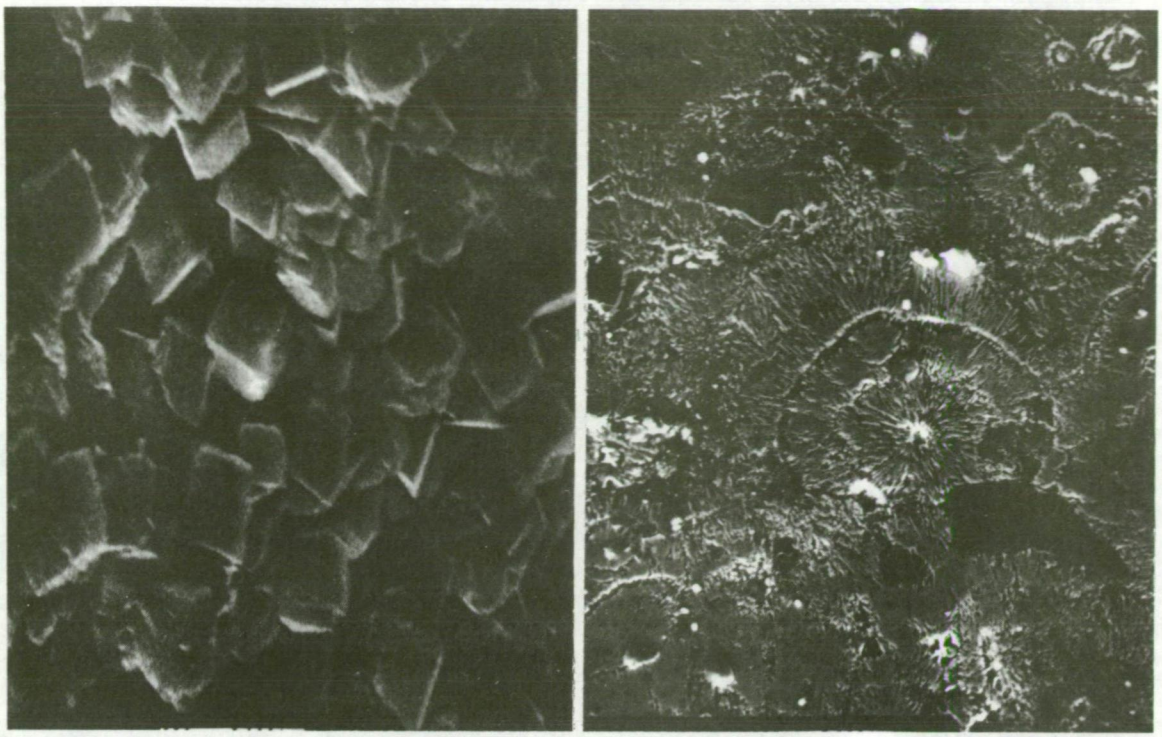

Figure (7.3) A: Rhombohedral haematite in a pipelet, 3150x. The rhombs are ca. 3μ per side.

B; Very rare pyrite in a relatively deeply formed pipelet, from ca. 5m depth,.7000x.

C: Colloform marcasite, the most common texture in relatively fresh pipelets, 300x, The dark grains are included sedimentary quartz clasts which are present in nearly all pipelets.

D: Fluted marcasite in a corroding pipelet, 500x. Note the holes to the left of the picture; they form an irregular ring about the much larger, more corroded central orifice.which has been separated from the gas flow. The inside of the orifice resembles (A) above.

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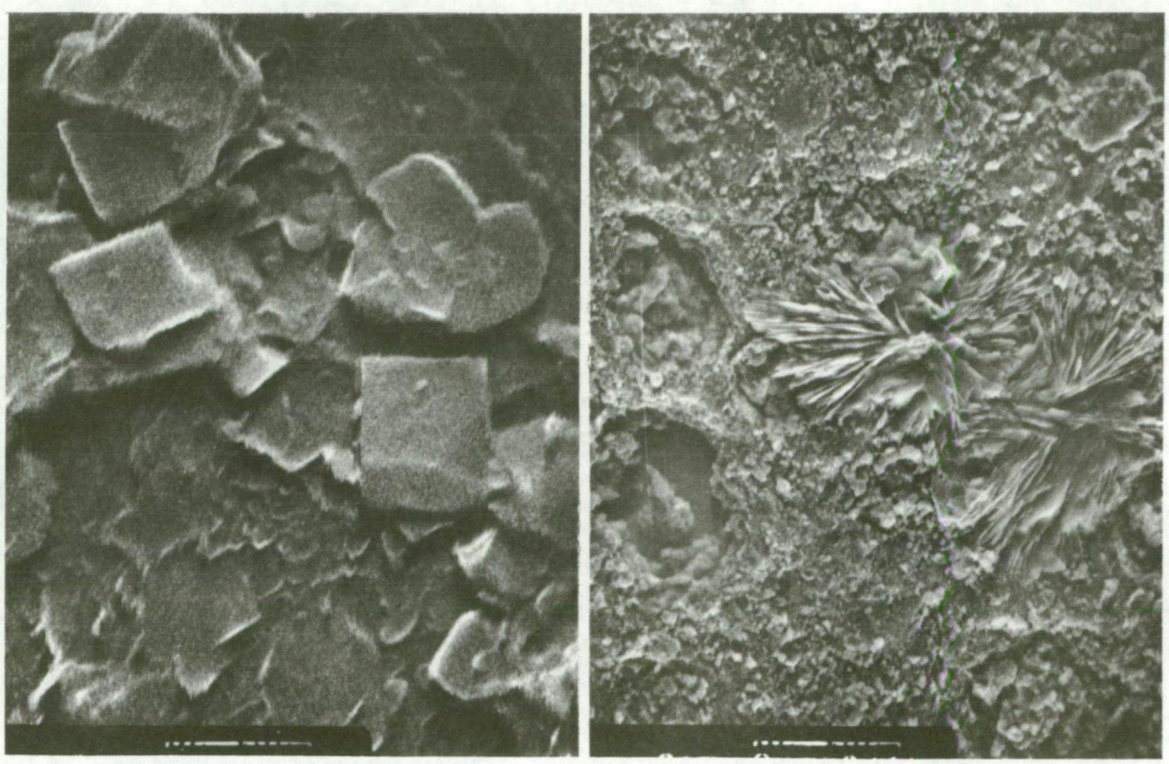

central thermal strip within the surface few metres. It is not found elsewhere in the basin. The mineral occurs in three characteristic morphological forms, which are peculiar to the environment and mode of formation. Each of the forms has the simple mineralogy: marcasite with inclusions of sedimentary clasts. The forms are:-

a. Pipelets
b. Nodules
c. Pseudomorphs

Pipelets are formed in warm to hot areas (≥ ca. 30°C) by rapid and direct chemical reaction where iron in ground-water meets a continuously rising column of sulphurous gas and marcasite encloses the gas stream (Figures (7.1) to (7.3)). Nodules form in slightly quieter conditions where gas percolates/disperses gently up through a porous and permeable medium in which water moves. The nodules are common in stream sediments and in sediments below the less ebullient parts of hot pools. Pseudomorphs replace vegetation debris lying in stream sediments near the water interface via a biogenic mechanism using sulphate and fresh ground-water. They form less rapidly than pipelets and most nodules; a 150 gm field speciment took 5 to 6 weeks to form under favourable conditions. The pseudomorphs, unlike the other two marcasite forms, may contain some intergrowths of pyrite.

a. Pipelets

They are tubes of external diameter 0.05 - 0.4 cm, internal diameter 0.02 - 0.15 cm and length 2 - 6.5 cm (Figures (7.1) to (7.4)). Fragments are common due to the brittle nature of the pipelets. The pipelets may display branching or rare explosive balloon-like shattering and regrowth on these breaks. In situ the pipelets are vertical, or less commonly sub-vertical, and the branches are usually near perpendicular at the tube, viz.:

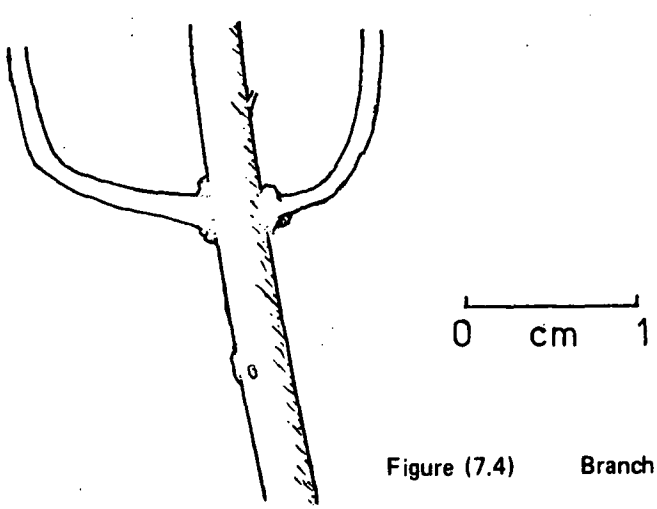

Figure (7.4) Branched Marcasite Pipelet

Pipelets occur only in wet ground where there is warm to hot thermal activity. The pipes are most prolific in the sediments of some thermal pools. They are found at the Tiger Bath (site 39), (site 52), the Cinnabar Bath (site 72) and site 30 in Figure (A.5), all near the edge of the central thermal strip magnetic anomaly (Jones, 1939); remnants can be found in most warm areas, particularly those richest in cinnabar.

The pipelets are a marcasite matrix with 0.1 to 1.5% clastic inclusions (mostly silica) and a thin black external tarnish (fresh FeS precipitate and in some cases meta-cinnabar). Extending from the centre of the pipelets are concentric sequences of colloform marcasite (Figures (7.1) to (7.3)). The size of the individual collform masses is 10^{-3} - 10^{-2} cm. Less commonly marcasite is present as tabular crystalline grains of 10^{-4} - 5 x 10^{-4} cm and rosettes up to 5 x 10^{-3} cm (Figure (7.2)). Commonly there is visible porosity (Figure (7.3)) which is greatest near the central orifice, about which there are annular arrays of ca. 1 - 3 x 10^{-4} cm diameter holes. Fresh pipelets readily desiccate when taken from their natural environment (Figure (7.2)).

Analyses are given in Table (A.4). No other sulphide minerals are found in the pipelets, in spite of the presence of up to several thousand parts per million mercury. Electron microprobe scanning showed that the mercury in unoxidized samples had no preferential sites. After an interval of 1½ to 2 days in oxidizing conditions the mercury showed a preference for the exposed surfaces.

b. Nodules

The nodules are readily found along and adjacent most of the length of the Tuwhakino Stream from the Tiger/Waima area to just below site 55 of Figure (A.5). Several hot baths near Tuwhakino Pond and at the Domain have minor occurrences. There is a strong preference for the south-eastern side of the Tuwhakino Stream, except near the Tiger Bath. Most nodules of contemporary origin are in the Waima/Tiger Bath area. The largest of all the specimens found was a 30 x 18 x 11 cm ragged mass dug out of the Tiger Bath in 1976 (Figure (7.1)). It had taken up to 3½ months to form (the Bath had been dug out prior to that interval). A 1 cm smooth nodule of cryptocrystalline marcasite which formed on submerged concrete in the quiescent Cinnabar Bath took up to 12 years to form. The former sample had associated cinnabar and the latter had none.

The nodules are commonly 0.5 to 2 cm in diameter and commonly contain 2 to 20% of unevenly distributed sediments grains (Table (A.4)). The shapes are irregular with common pitting and ragged embayment. Most nodules have a thin black skin, under which is a matrix of mostly microcrystalline granular marcasite with sediment inclusions. Very rare euhedral pyrite was found in a few nodules and was probably part

of the included sediments. Colloform textures are less common than in the pipelets except for the outer 2 to 3 mm of most specimens.

Where the marcasite is granular the grains are commonly 1 - 2 x 10^{-3} cm in diameter. The granular texture is not resolvable or very difficult to resolve under the electron microscope without etching. Similar to the pipelets, the nodules prefer conditions of warm sulphurous wet ground, however nodules generally grow in areas of less vigorous gas action and are far more common in stream sediment environments than the pipelets.

c. Pseudomorphs

Observed in the area of the Tiger Bath was the replacement of vegetation debris by marcasite, and in some cases, by pyrite also. The replacement process was confined to the streams and occurred at the sediment - water interface. The materials replaced were modern tea-tree and ancient kauri, both wood and charcoal. Most of the observed specimens had been large twigs of 1 - 1.5 cm diameter and 7 - 13 cm long. The marcasite (Figure (7.5)) is dull to dark grey externally and has an internal crystalline nature usually visible to the unaided eye. The outside commonly bears subtle striations reminiscent of the original wood grain, however there are no distinguishing patterns internally.

The marcasite is usually 0.05 to 1 mm tabular to almost cubic grains with no inclusions. Grains are euhedral and up to 0.3 mm. (Rarely specimens have shiny golden pyrite: Occurrences of pyrite generally replace charcoal, and are among the more deeply buried specimens and mostly replace the outer part of the specimens.) In very rare circumstances only pale cinnabar colouring is present on the outside, yet mercury is present in similar quantities to that in the nodules and pipelets. (No bright coatings were seen on any fresh pseudomorphs.) In many cases the total mercury concentration was slightly higher, and destruction of the pseudomorphs by oxidizing acid digestions showed the presence of cinnabar as extremely fine grains.

The environment of formation is stream water with minor thermal-bath overflow passing over warm gaseous anoxic ground, where pH is about 6.5 to 5 in the muddy silt just below the usually more acid stream water. Twigs jutting up into the acid water failed to be replaced by marcasite above the sediment interface. Consequently samples with marcasite at one end, relatively normal wood at the other and a sharp boundary between can be obtained. In adjacent areas (now not in the stream) cinnabar-rich sediments with haematite and/or limonite, sulphur and minor organic debris commonly occur with pseudomorphed material, but within the active environ-

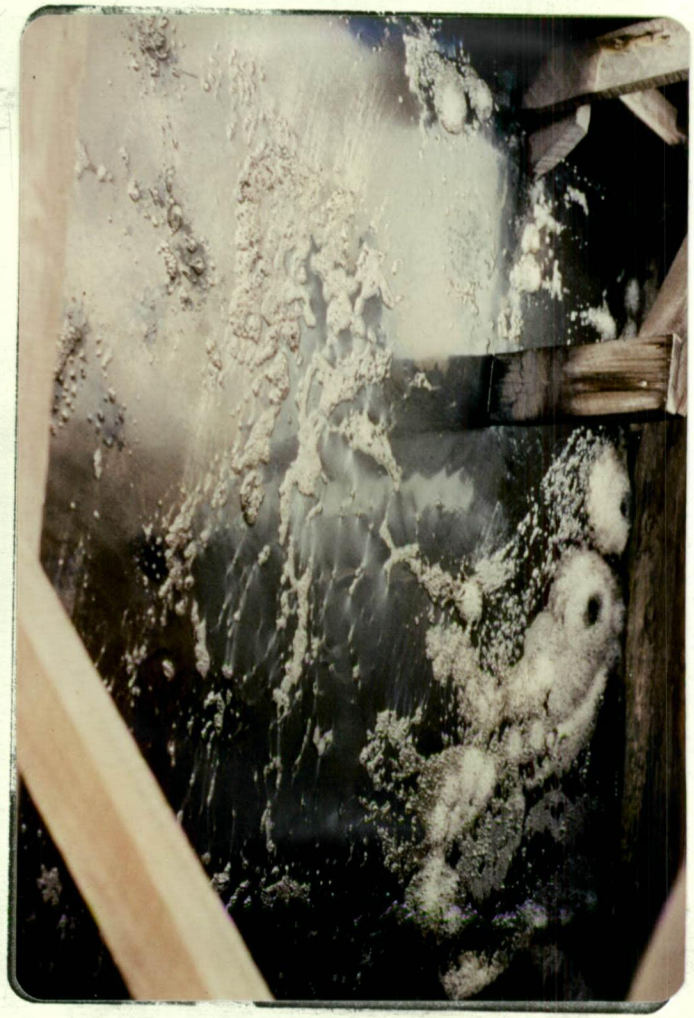

Figure (7.5) A: An oily pyrite scum on the water of the Scotsman Bath near Tuwhakino Pond and Jubilee Bath. The latter is the hottest pool in the entire basin. (1/8x). B: A pyrite pseudomorph grown in the laboratory under simulated field conditions; 3x. C: Marcasite partially pseudomorphing wood from the upper Tuwhakino Stream adjacent to the Tiger Bath; 2x. The remnant wood was exposed in the stream-water where as the marcasite portion sat in the sediments below the running water, some sediments adhere to the left.

ment of formation, although sulphur is relatively common, cinnabar and haematite are relatively scarce and variable.

(7.3) PYRITE

The mineral is rare in all surface environments and only occurs abundantly along the subterranean edge of the basalt bordering the Tuwhakino area from ca. 5 m below the surface (Jones, 1939). Griffiths (1898) showed the presence of pyrite just west of Lake Waiparaheke, but does not describe it: none was located during field work although goethite, limonite and minor sulphur were found. No significant iron mineral occurrences have been found in the northern thermal strip, and as with all the other iron minerals pyrite is only found adjacent to basalt in the Ngawha Basin.

Only in the Tuwhakino area is pyrite found associated with current thermal activity, but it is very rare in cinnabar occurrences (< 0.01%). It is found as 0.5 - 1.25 mm single euhedral cubes in sediments near several very gaseously active fumaroles, and it constitutes a large part of the thin oily scum on the Tranquility and the Scotsman Baths (site 72 of Figure (A.5)) near Tuwhakino Pond (Figure (7.5)). For the baths it appears that the pyrite is physically transported from below. The occurrence of the pyrite cubes in sediments (and cinnabar deposits) is believed to have a similar origin: transport for several metres due to fluid ebullience since small quantities of the fresh pyrite appear in environments which only favour the oxidation of it and marcasite, e.g. Waima.

There is not a direct relationship between any pyrite and cinnabar deposition. Generally pyrite has about an order of magnitude lower mercury concentrations (ca. 15 - 200 ppm) than marcasite, and pyrite does not have or form cinnabar coatings.

(7.4) HAEMATITE

Haematite is purely a surface mineral, and the majority of it is secondary. It occurs in areas of sulphurous thermal activity close to basalt, and does not occur more than 2 - 3 m below the surface. The main occurrences are in the Tuwhakino area, the lowermost of the Sulphur Ponds and Waitotera Pond. The mineral is most abundant in and near cinnabar deposits, but scarce in ground currently depositing cinnabar. Generally the locations are the same as those for marcasite, except that marcasite favours greater depths, warmer ground and less acid conditions.

The haematite is present as micromammillary and concretionary crusts and rhombohedral grains in pipelets, nodules and sediments. Only in some nodules does there appear to be any primary haematite. Some crusts are partially primary, but they are not envolved in any hydrothermal process. The haematite viewed via an unaided eye or hand lens has an earthy nature, except in some crusts under a hand lens where it is red-brown and has a metallic to submetallic lustre, and appears resinous without the lens. Usually the fabric is entirely haematite. In certain pipelets and nodules marcasite and haematite may alternate, usually haematite is the less common mineral and is entirely rhombohedral of side ca. 2×10^{-4} cm (Figure (7.3)).

Contrasting marcasite, haematite contains very little mercury ($\leqslant$ 5 ppm), yet it may be intimately mixed with cinnabar, e.g. at sites 37, 31 and 52. (In fact it is the oxidized/oxidizing marcasite which most commonly has visible cinnabar attached). pH in the haematite depositing areas are usually acid, ca. 4 or less.

Goethite and Limonite

The main significance of these minerals is that they occur where there is little sulphur, and a plentiful supply of iron. They correlate with the absence of thermal activity and the presence of basalt. The two minerals also form in less acid conditions than haematite.

Limonite occurs along most of the southern side of the central thermal zone, along most of the Te Pukoro Stream, in water seepages along the northern side of Waiparaheke to Ngamokaikai and in several tributaries of the Te Pukoro which pass under Highway 12. Goethite was only found underground half-way along the northern side of Waiparaheke Pond. Neither mineral has any particular association with other minerals, and deposition pH's range from 5.5 to 7. Mercury concentrations are commonly below 3 ppm, and very rarely up to ca. 150 ppm close to vigorous thermal activity.

(7.6) MERCURY

Mercury is known to occur as three minerals in the Ngawha Basin; cinnabar, native mercury and metacinnabar. Metacinnabar is rare. The mercury minerals have been found only in the western half of the central thermal zone and at Waitotera Pond, although mercury vapour is readily detectable in gases from all three thermal zones. Economic deposition has happened only in the central thermal zone, where current deposition of cinnabar and elemental mercury have been observed.

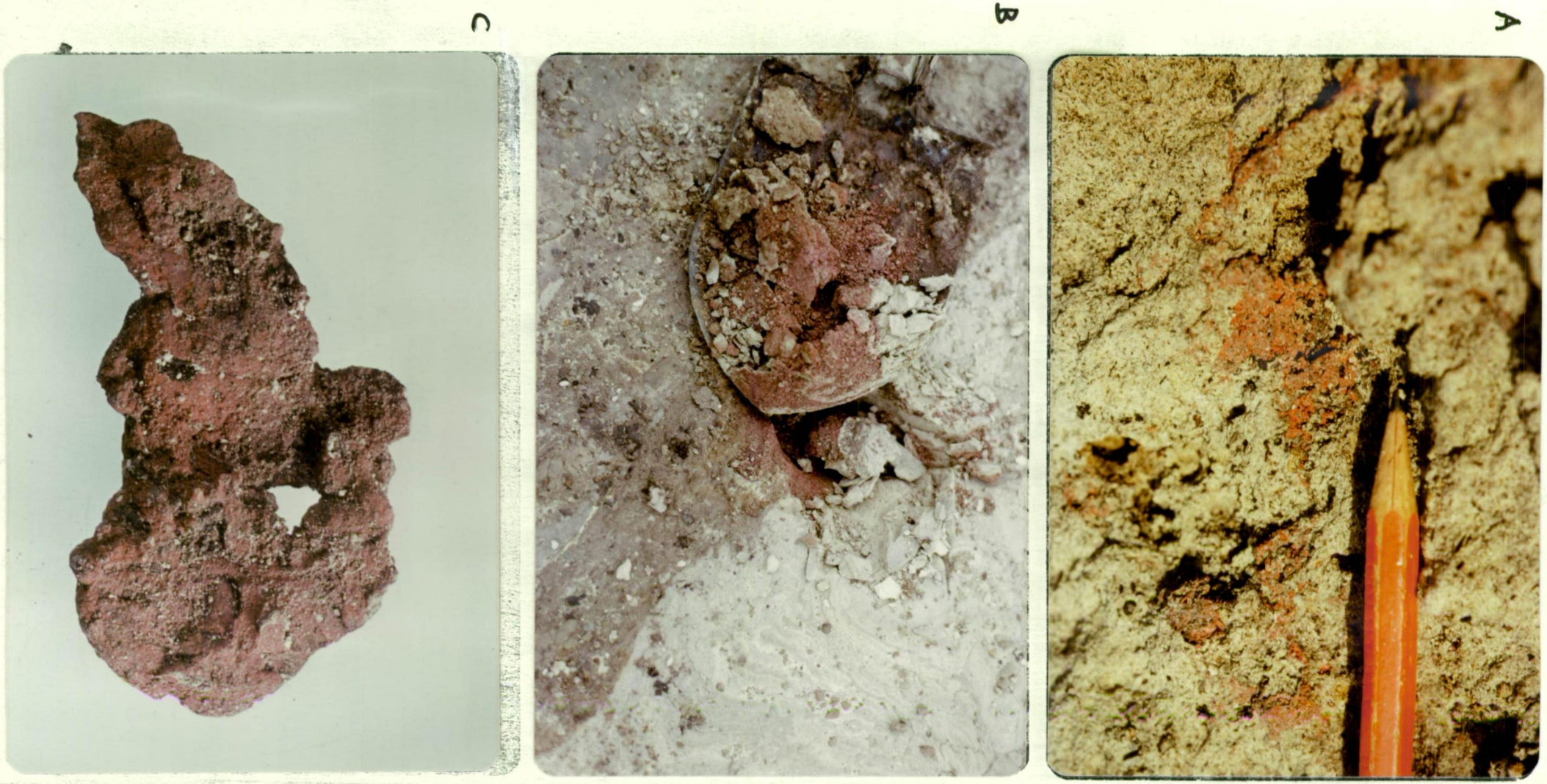

Figure (7.6) A: Cinnabar-cemented stream sediments; 3/2x. Note the many flecks of dark brown organic material in the sediments. The cinnabar-rich parts of the sediments are very commonly pulverescent. B: Cinnabar in ancient fine-grained and sulphurous pool sediments and haematitic/limonitic fine to medium-grained sediments; 1/3x. The richest cinnabar is in the iron-rich sediments which are relatively sulphur-poor. C: Cinnabar in dominantly coarse-grained sediments with only minor haematite in an area of exposed stream sediments and pseudomorph oxidation; 7/5x, cf. Figure (7.7). The bulk of the material, apart from the cinnabar, is quartz.

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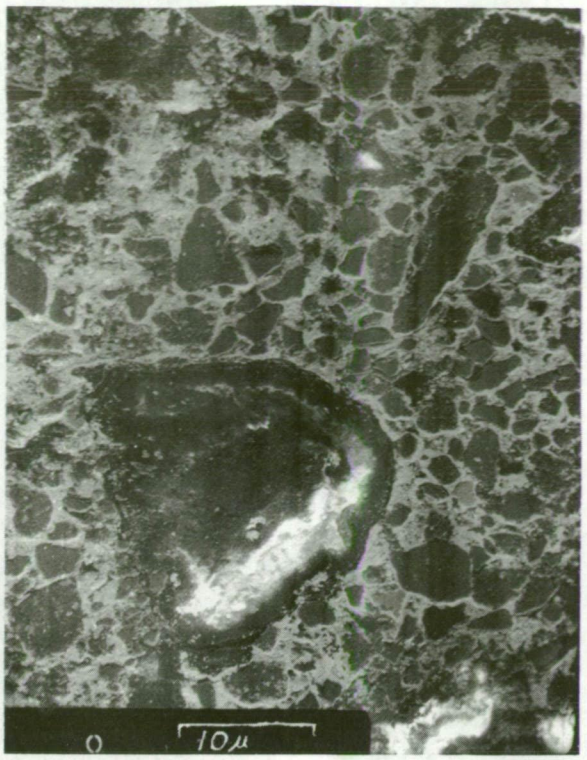


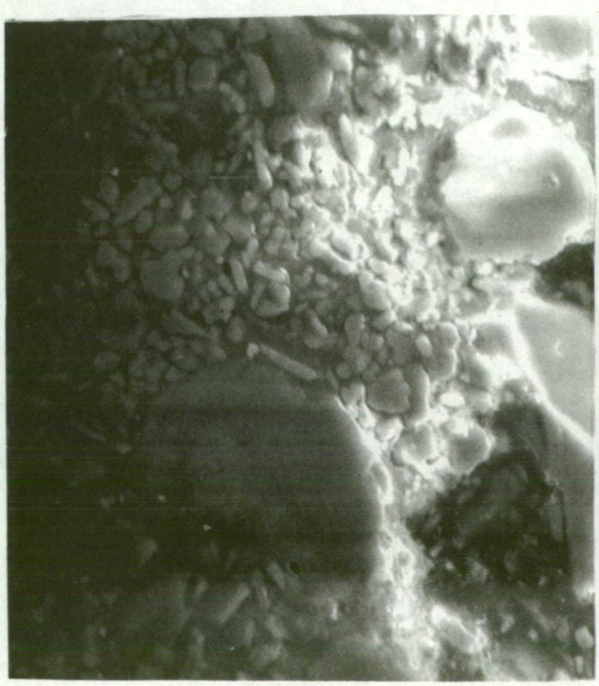
Figure (7.7) A: Cinnabar in old stream sediments, 150x. The large rimmed grains are quartz. Minor alunite and organic material are also present as the 'amorphous' white patches and the very dark (non-shadow) areas respectively.

B: Irregular tabular cinnabar grains in hot pool sediments, 1000x.

C: Cinnabar-rich hot pool sediments, 50x. The darker grains are mostly quartz. It is the intergranular / matrix cinnabar which is depicted in (B) above.

D: Mercury squeezed from dried sediments in the upper Tuwhakino area near profile B. The sediments are carbonaceous and contain up to 10% mercury, including cinnabar as depicted in Figure (7.10).

B



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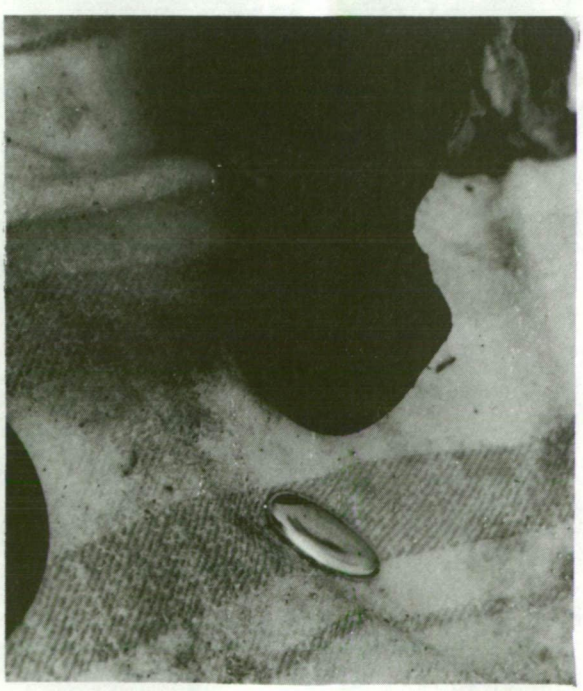


(7.7) CINNABAR

Cinnabar occurs throughout the area from Tuwhakino Pond to the Waima - Tiger Bath area in concentrations up to ca. 20% (Table (A.10)), and around most of Waitotera Pond except its western side. Generally cinnabar comprises only 0.1 to 5% of mercury-rich materials and is mostly present as a partial interstitial filling in sediments (Figure (7.6)). In coarse sediments (sands) it commonly adheres to various grains in the form of earthy granules; a similar unresolvable earthy form is present in the bulk of the fine grain sediment deposits. Very rarely are any veins of cinnabar present.

The cinnabar is present as cryptocrystalline to rare 1.5×10^{-3} cm approximately rhomhedral grains (Figure (7.7)), and in all but a few special cases (on organic matter) cinnabar grains were unresolvable on an electron-microscope at 10^4 magnification. In samples where cinnabar formed the matrix, some cinnabar was present as irregular and almost tabular granules of about 2 to 5×10^{-4} cm diameter.

Within a deposit cinnabar may have direct affiliations with marcasite and organic materials (Figures (7.8) and (7.9)). It is common as coatings on wood, peat and charcoal fragments. The coating is usually 0.1 - 0.5 mm thick, with rare thick occurrences on very charred wood. Peat is least associated with coatings. The coating on marcasite may appear virtually part of the marcasite where it is thin, and where it is thick (0.05 to 0.2 mm), it may be strongly bonded or able to be 'wiped-off' with difficulty. In general cinnabar formed on pipelets is fairly evenly distributed and tightly bound whereas that on nodules adheres poorly as unevenly distributed granules, possibly with a thin patch of well bound cinnabar. Cinnabar is particularly associable with areas of haematitic nodules and pipelets. Exposure of pipelets at the Tiger Bath was found to cause cinnabar to appear on the outside in 2 days (Figure (7.8)), the cinnabar was very firmly part of the pipelet, and about 0.1 mm thick. In no case was cinnabar intergrown with other minerals.

a. Cinnabar Associations

The common associations with cinnabar deposits at Ngawha Springs are:-

1. Cinnabar disseminated in coarse grained sediments cemented by alunite and sulphur (to a lesser extent). Contained in the interstitial matrix is sulphur, limonite haematite, dark organic material and rarely corroding marcasite. (Limonite is mostly restricted to the inside and the less alunised zones and bands of the sediments).

Figure (7.8) A: Irregular coherent nodules of marcasite, cinnabar, native mercury and minor haematite; 1.2x. The sample was found in high level geothermal sediments in an area without current geothermal activity and about three metres above the present water-table; 1.2x. B: Cinnabar which was observed to form on charcoal about 1.5m north of profile A; ca. 0.6x. The cinnabar is not related to any known bacterial action. It forms subaerially during non-sunny periods probably due to the reaction of adsorbed mercury and sulphur on the surface. C: The loose surface material near the centre of the photograph was taken from the Tiger Bath two days prior to photographing, and the red to purplish-red blooms developed in that time interval; 1/2x. Most of the grey material is marcasite, the black matter is organic and almost entirely charred and water-logged kauri.

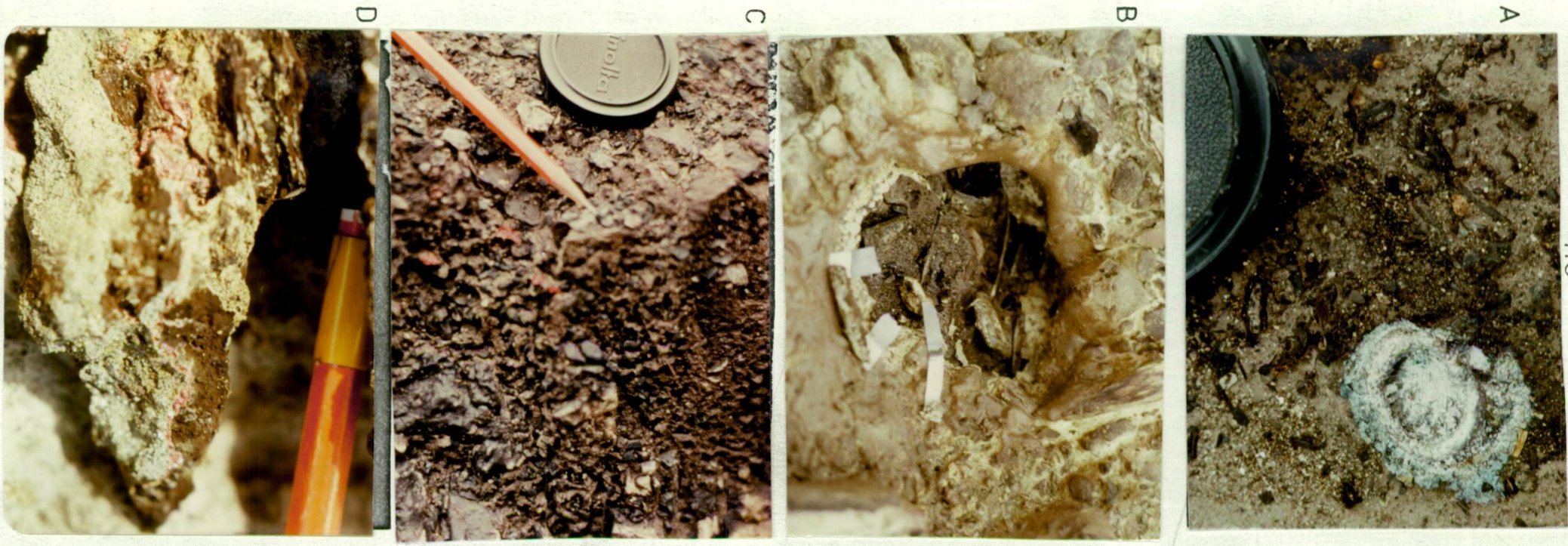


Figure (7.9) A: Condensed elemental mercury about a small warm fumarole seeping gas at ca. 28°C; 0.8x. B: Elemental mercury collecting on fresh detection papers (Davey and van Moort, 1974) at theorifice of a fumarole, ca. 27°C. Note the sulphur-cemented sediments; 1/2x. C: Cinnabar associated with tar on the banks of the Tuwhakino Stream; 1/2x. D: Cinnabar coating vuggs and 'lithology' boundaries in soil which was formed prior to the outbreak of local sulphurous thermal activity. The yellow is sulphur-with minor alunite-cemented sands which have surrounded the old soil mass; 1.3x.

Figure (7.10) A: Copper rapidly coated an iron spade dipped into the Tiger Bath in 1973; 1/3x. B: Sediments containing vegetation debris interleaved with cinnabar near profile B; 1.2x. C: Geothermal sediments consisting of dominantly sulphur-cemented brecciated 'lake sediments' near the Tiger Bath; ca. 1/10x.

2. Cinnabar disseminated in silty muds which are oily, and contain charcoal, peat, tree trunks (commonly charred), sulphur and marcasite (Figure (7.10)).

3. Local cinnabar-rich fine sediments with little or no organic matter, no iron minerals and no sulphur (Figure (7.6)).

In active areas of cinnabar deposition, the coarse grain sediments are stream sediments in flat areas with strong water seepage and warm gaseous thermal emanations. The fine grain sediments are usually pool sediments and stream areas which have very slow water movement. A few vigorously ebullient hot pools have cinnabar in localized coarse sediments. The area where by far most of the current cinnabar deposition was observed is in the Waima - Tiger Bath area at the western extremity of zone 2.

General associations with current cinnabar deposition are the presence of:-

i Plentiful sulphurous (H_2S) gas emanations.
ii Warm to hot temperatures ($\geqslant$ ca. 30° C).
iii Acidic water (ca. $1 < pH \leqslant$ ca. 5).
iv Organic condensates and forest debris.
v. Ammonical gases (and ammaugnite occasionally).
vi Sulphur.
vii Relatively fresh water or relatively chloride rich ($\geqslant$ 750 ppm) with sulphate
viii Marcasite.
ix Not below 10 m depth.
x Mercury-rich gas ($\geqslant$ 50 μg/l Hg^o).
xi Reworked sediments.

In the case of non-depositing sites the associations with cinnabar are the same, except that any one or more of associations i, ii, iii, v, vii, viii and x may be absent. However at all occurrences of cinnabar the associations can be found no more than a few metres away. Haematite is very commonly associated with cinnabar occurrences in areas of moribund thermal activity. In several localities with many buried tree trunks, the distinctive odour of dimethyl-sulphoxide was present in exposures e.g. site 42 of Figure (A.10).

(7.8) NATIVE MERCURY

Native mercury is visible throughout the western half of the central thermal

Figure (7.11) A: Elemental mercury adsorbed onto brass and iron from the air near the Tiger Bath. B: Elemental mercury lining the joints of the banks of the upper Tuwhakino Stream. C: An elemental mercury seepage in a small tributary of the Tuwhakino Stream; 1/6x. (There are many similar seepages along the stream, especially on the southern shores.

zone, but was not observed elsewhere in spite of high concentrations of the element (Tables (A.10), (A.2) and (A.3). Unlike cinnabar the element is more evenly and widely spread. It collects on many metals (especially copper) during still cool periods even in areas not near major warm to hot fumaroles. In winter it is particularly prevalent in joints of rocks and soils (Figure (7.11)) and around dry surface emanations, during summer it remains prevalent near major fumaroles (Figures (7.9) and (7.11)).

The highest concentrations are associated with areas of warm to hot fumaroles ($\geqslant 25°C$). Consequently it is strongly associated with cinnabar occurrences. (It was also observed to form as a film on cinnabar exposed to sunlight in a few instances. The element formed by photolysis of cinnabar. However this represents an insignificant source of the element). In the field it has few other noteworthy correlations.

Chiefly mercury is a condensate and is present as coatings and droplets. Most coatings are not visible, but they may be shown to be present by slowly immersing the material into water, where some of the mercury forms a very thin visible film on the water surface. Occasionally similar films of mercury also appear on natural water seepages. Droplets of mercury are mainly restricted to below 0.5 m depth in areas of at least some weak warm thermal activity, and a frequent association is oil. The droplets are confined to mainly fine-grained sediments which are wet. The only exception found was a few grams of native mercury closely associated with a large nodule of marcasite in dry silt near site 31 of Figure (A.10).

Films of mercury are usually a dull to pale grey silver, whilst droplets commonly have a bright metallic lustre. Coatings range up to about 0.05 mm thick, and very rarely to 0.2 mm on sulphide minerals. Droplets up to ca. 3 mm were found, but most were ca. 0.5 mm or less.

(7.9) METACINNABAR

It is rarely found as black coherent coating on fresh pipelets from hot baths in the Tiger - Waima area.

(7.10) ARSENIC

Realgar was found at one location (profile D), and orpiment was found at two sites (profiles D and B). In general arsenic has very low concentrations throughout the thermal zones and environs (Table (A.5)). However 0.01 and 0.2 ppm have

been reported in the water from the Jubilee Bath (Fleming, 1945).

At profile D, realgar was present as 1 mm long acicular translucent crystals dispersed through a sediment matrix above a small fissure. Towards the upper part of the ca. 30 cm interval of occurrence were small 1 - 2 mm granules of pulverulent orange orpiment, scattered randomly. The average arsenic concentration of the 30 cm interval was ca. 1.2% with up to 5% locally.

Orpiment also occurred as a veinlike concentration in puggy mud at profile site B. The orpiment was brownish orange in a 0.8 cm wide curvaceous band of arsenic-rich wet colloidal sediments and was evenly dispersed. Except for the immediate vein area, much of the locality has very high mercury concentrations, and included cinnabar coatings on joints in the peaty earth above the orpiment which was at ca. 65 cm depth.

Antimony

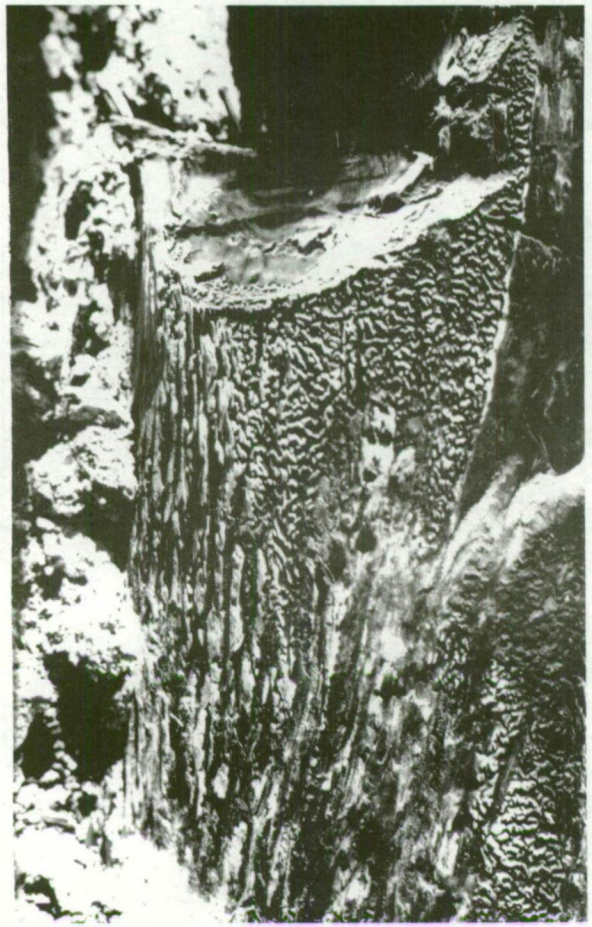
Minor metastibnite was found at profile site L. It occurred as purplish black 'dust' in a dominantly coarse-grained sediment horizon as interstitial filling. No other antimony mineral occurrences were found, however many of the stream sediment and hot pool sediments analysed in the Tuwhakino area showed the presence of about 1 - 2% antimony. Water analyses have not shown the presence of soluble antimony (detection limit 0.5 ppm).

Sulphur

Colloidal precipitated sulphur occurs at all thermally active centres, and several moribund centres. In warm areas it may also cement old geothermal sediments and form veins and crusts along gas vents. The bulk of the sulphur is in large pools of cool ebullient gas activity, such as the Sulphur Pool, and parts of Waitotera and Waiparaheke Ponds. Very sulphurous sediments (20 - 90% S) do not coincide with cinnabar deposition. However sulphur is rarely absent from cinnabar deposits. Colloidal sulphur (in pools and streams) is much paler than the vein and crust sulphur (in 'dry' gas vents and the adjacent 'dry' permeable ground), which are pale orange-yellows and yellows. Except in some deep pools and along small gas vents sulphur rarely occurs below 2 m depth.

During drizzle conscpicuous colloidal sulphur may form, for instance the stream passing through Waima was observed to become milky during rain. There was also an increase in acidity due to sulphate from the oxidation of sulphide. In several areas of exposed stream sediments (e.g. Figure (4.6)) many subregular bands of sulphur-rich sediments occur, and commonly such sediment masses also contain significant quantities of cinnabar but not so much in the sulphurous bands. It is probable that the sulphur-bands have formed by the prior-mentioned observation during rain.

C



B

A

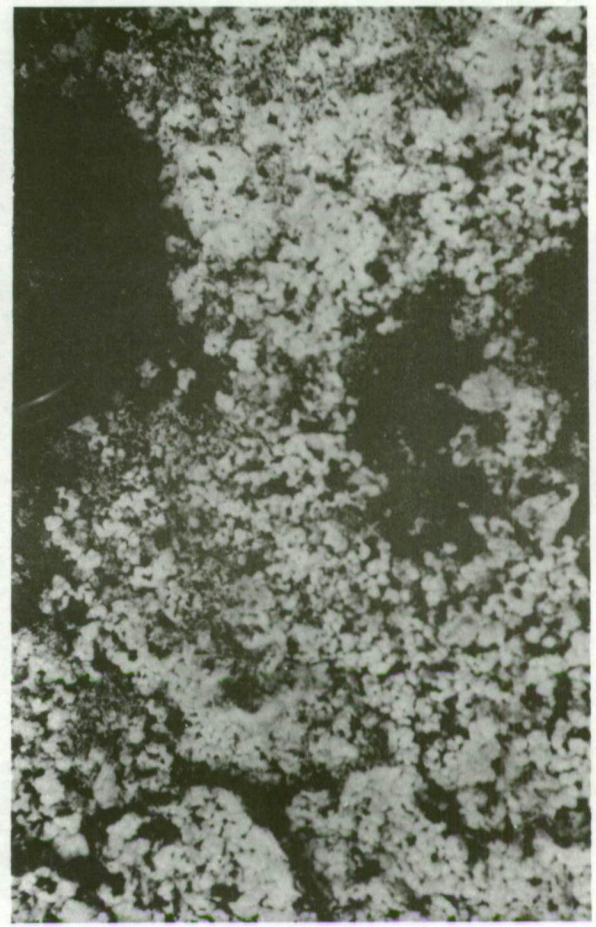


Figure (7.12) A: Ammaugnite efflorescence on warm sulphurous ground in the Waima area, 5/7x. The ammaugnite, $(NH_4)_2SO_4$, forms from the partial oxidation of the geothermal gas which contains ammonia and hydrogen sulphide. B: Iron which originates from ground-waters oxidizing on entry into the Tuwhakino Stream as the stream enters the Domain area. C: Alunite impregnating the outer few centimetres of a tree buried in sulpur and alunite cemented sediments. The tree is one of many felled by the outbreak of geothermal activity and associated sediment sapping. The trees have been preserved by the accompanying thermal emissions and many give radiocarbon-14 dates of about 6850 Y.B.P..

CHAPTER EIGHT MECHANISMS OF OBSERVED DEPOSITION REACTIONS

Both cinnabar and marcasite have been observed forming in the upper Tuwhakino area. Cinnabar was observed to form on charcoal, in stream sediments, in thermal pool sediments and on marcasite, and marcasite was observed to form in stream and pool sediments.

(8.1) CINNABAR DEPOSITION

During and just after rain, cinnabar conspicuously forms in streams which have sulphurous gas activity and are in areas of warm to hot thermally active ground (ca. $\geqslant$ 30°C) (Davey, 1974). Colloidal sulphur also forms in the streams, and pH commonly falls by 2 - 3 units (on one occasion a pH near 1.5 was measured during drizzle). Contemporaneous with the appearance of cinnabar is 'iron-stained' water, haematite and rarely pyrolusite (Figure (7.12)).

On exposure to the local air or streams, pipelets and some nodules from several hot pools in the Tiger Bath area formed cinnabar during 2 - 3 days (Figure (7.8)).

At site 42 of Figure (A.10), Mound A, cinnabar was also observed to coat charcoal during prolonged overcast weather. Mound A is 'dry' and only a weak gas supply passes up through the relatively elevated ground.

In hot ebullient pools ground containing relatively high aqueous chloride concentrations ($\geqslant$ 500 ppm Cl^-), very fine dispersed cinnabar forms at a slow but near continuous rate (e.g. Tiger Bath and in hot wet ground at Waima). However this cinnabar appears to be restricted to areas with mixing waters, (e.g. no cinnabar was found to form in the Jubilee Bath, the hottest of the pools).

Since elemental mercury is the only feasible source of mercury (since other species are not sufficiently soluble nor were they detectable), there must be a reaction which forms Hg II. The observed cinnabar depositions all indicate that they occur in environments which have contact with either air or surface waters (which contain dissolved air). The common occurrence of elemental sulphur (with cinnabar) strongly indicates that oxidation of H_2S occurs (hence $Eh \geqslant 0$ and $pH \leqslant 4$), and the abundant HSO_4^- in most pools implies $Eh \geqslant 0.2$ at times. In one stream with cinnabar deposition, an Eh of over 0.9 volts (oxidizing) was calculated (Davey, 1974), hence significant quantities of oxygen were present.

For the reaction $Hg \rightleftharpoons Hg^{2+} + 2e^-$ the standard electrode potential (E°_1) is 0.815v (Weast, 1976). Therefore it is probable that mercury can be oxidized by the reaction:-

$$2H_2O \rightleftharpoons O_2\,(g) + 4H^+ + 4e^- \qquad \ldots E^\circ_2$$

Under the conditions at Ngawha Springs the potentials become Σ°_1 = ca. 0.5 volts for a transient $[Hg^{2+}] = 10^{-10}$ M, and Σ°_2 = ca. 0.95 volts for pH = 3 - 5 and O_2 = 10^{-4} - 10^{-7} M. Hence the oxidation of mercury is thermodynamically spontaneous. Laboratory experiments were carried (out with and without oxygen) and showed that the reaction does occur.

Since the oxidation reactions occur in mixed open systems (non-equilibrium), and H_2S is available as well as oxygen, once formed, any Hg^{2+} soon yields the very insoluble species HgS. The presence of Cl^- is known to enhance the oxidation of mercury (Wilkinson, 1972), hence the oxidation may occur at the low potentials of many hot pools.

For the case of the surface appearances of cinnabar (on charcoal and marcasite) adsorbed mercury oxidizes then reacts with H_2S from the local environment albeit aqueous or aerial.

(8.2) MARCASITE AND CINNABAR DEPOSITION

Marcasite forms where ground-waters from basaltic areas encounter relatively fresh thermal fluids. Pipelets form about rising gas and encase it. Frequently the pipes choke or block the gas flow, and another path is taken which also becomes encased in marcasite. During very oxidizing periods (e.g. during rain) haematite may form hence many pipelets display an alternating anular growth structure (Figure (7.1)). Large masses of marcasite with minor cinnabar were observed to form in the Tiger Bath muds adjacent the main gas orifices. Marcasite deposition is due to the direct interaction of geothermal H_2S and iron in ground-water from basalt. The marcasite rarely forms in waters where pH< 4.

When the marcasite is exposed to erosion it corrodes to both haematite (Figure (7.3)) and transient aqueous Fe^{2+} which is carried off and oxidized in the streams. Cinnabar is left behind and increases in concentration as the erosion and corrosion continue (Figure (7.7)). The density of cinnabar (8.1 gm/cm^3) also reduces the risk of transport as detrital material. Hence some sediments have become very rich

A B

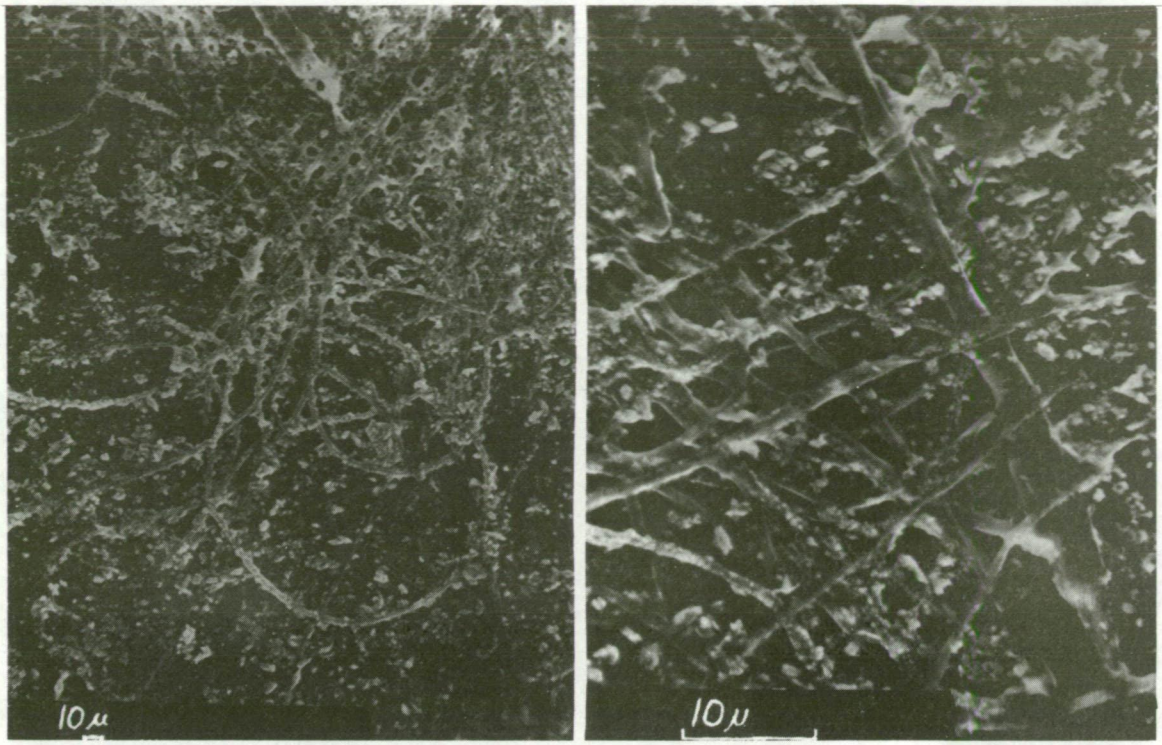
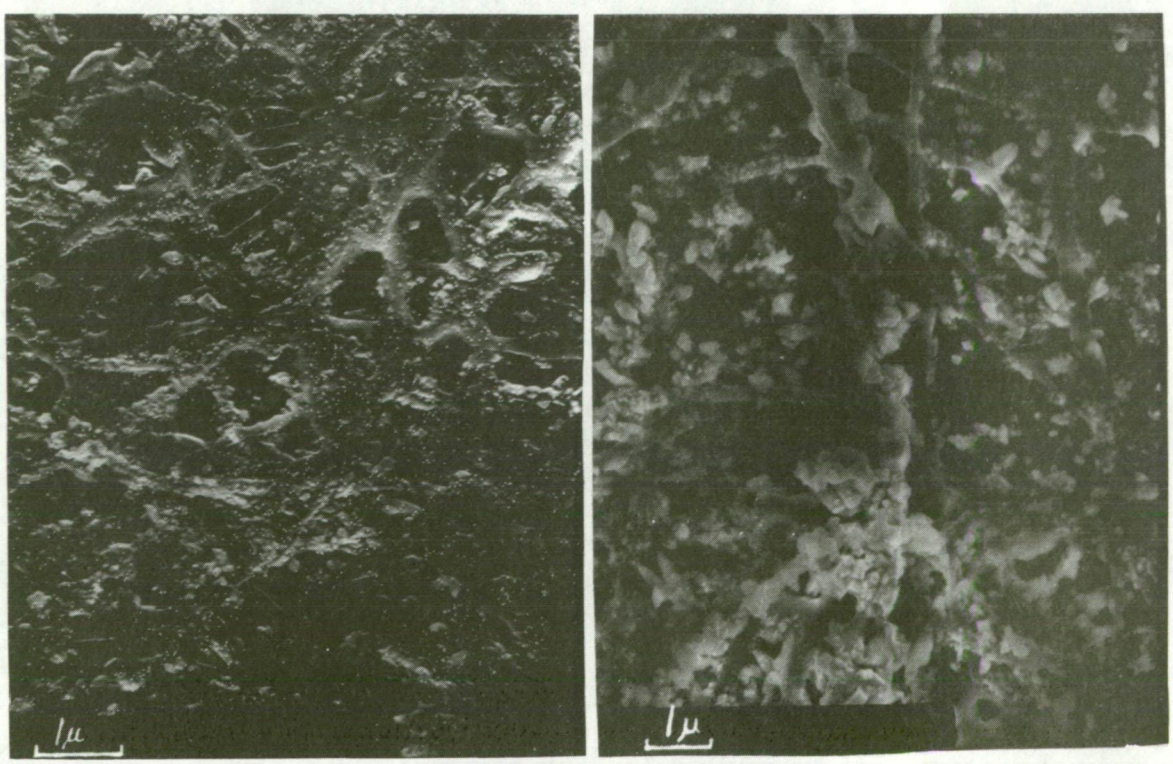


Figure (8.1) A: Non-thermophyllic filamentous sulphate reducing bacteria responsible for the iron sulphide pseudomorphing of organic materials.

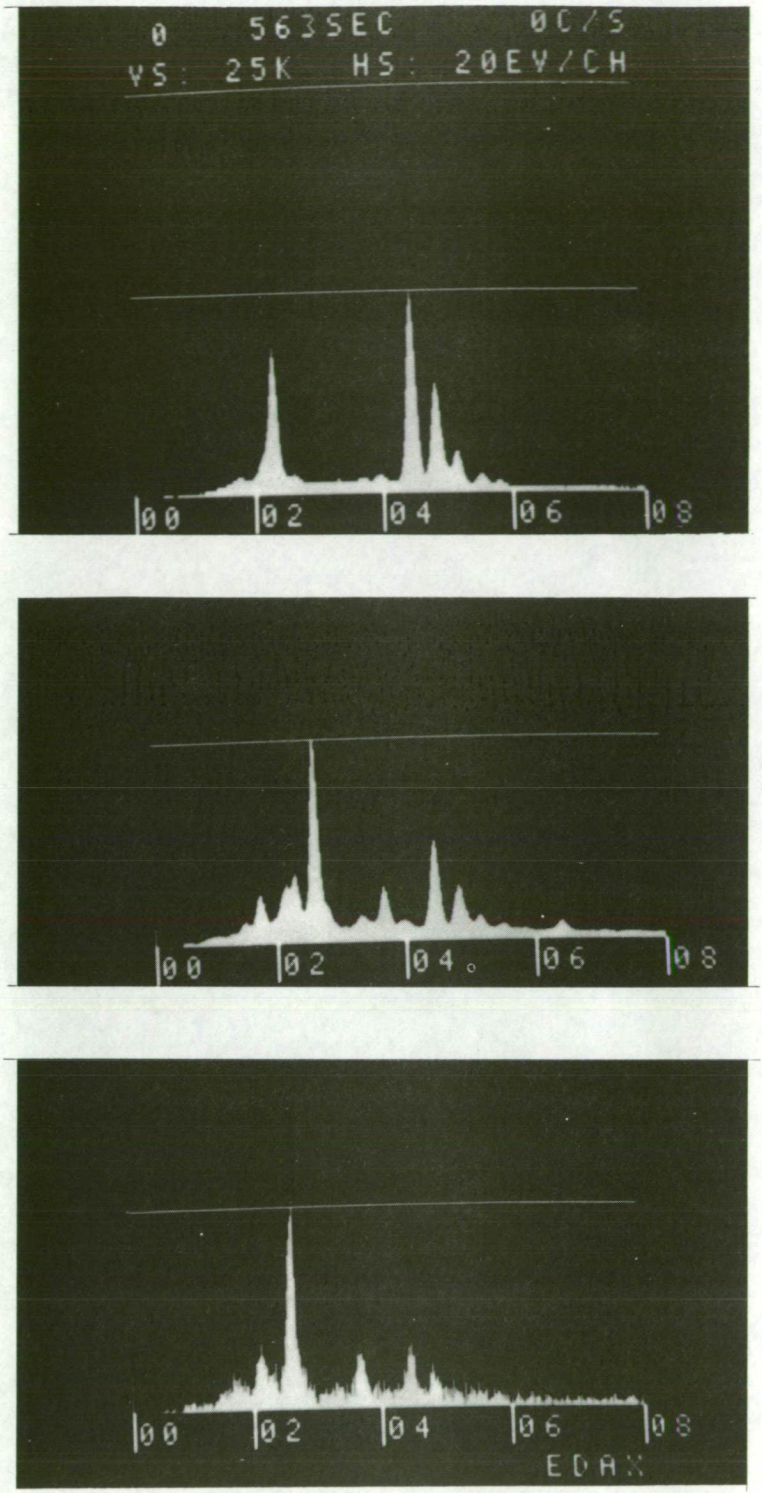
B: Bacteria as per (A), 500x. The interfilament material, particularly in the top right of the picture is clasts of silica.

C: The filamentous Bacteria at 800x with an X-ray scan for sulphur displayed as dots of light. The analysis shows that the bacteria have 'sulphur-rich' areas, and infact have nearly all the sulpur in the entire specimen.

D: FeS_2 forming on the bacteria, analysis is given in Table (A.17). Note that the pyrite grows only on the bacteria, the bulk of the other material in the electron micrograph is silica as shown in (B). Figure (7.5) shows the pyrite grown from the depicted specimen. Magnification is 1000x.



C D



A

B

C

Figure (8.2) The above are X-ray spectra of solutions in a run with the pseudomorphing bacteria The spectra demonstrate the gradual consumption of sulphate sulphur from $BaSO_4$ to produce FeS_2 in the presence of a slightly acid buffer solution. As the sulphur is consumed the main barium salt present chages to the chloride. The analyses for A,B and C are those numbered 5, 8 and 10 in Table (A.17) respectively. The main peaks in the above spectra are S, 2.3; Cl, 2.7 and Ba, 4.6 units.

in cinnabar and contain only minor haematite (Figure (7.6)). The accumulation of cinnabar also indicates that the possible oxidation of cinnabar in the presence of ferric ions (Burkstaller, McCarty and Parks, 1975) is much slower than the formation of cinnabar.

(8.3) PSEUDOMORPHS

Both mercury and iron are present in the pseudomorphs of organic materials which are formed by non-thermophyllic filamentous sulphate-reducing bacteria in streams containing overflow from thermal baths (Figures (7.5) and (8.1)).

Samples of water, wood and partially replaced wood contain the bacteria which was cultured and used to check that it was responsible for the pseudomorphing process. Culturing was carried out in closed vessels with natural waters from Ngawha and synthetic solutions. To the solutions were added combinations of sterile agar agar, glucose, gelatin, $CaSO_4$ or $BaSO_4$, buffers, dilute HCl, $FeSO_4$ and wood to optimise the growth of the bacteria and check its reactions. In the presence of glucose, gelatin and $CaSO_4$ mats of bacteria could be produced.

The bacteria in the mat were the same as found in the Ngawha Springs 'pseudomorph environments', and were produced almost free of other bacteria. Near neutral solutions were required ($8 \geqslant pH > 4.5$). Pyrite was able to be grown from synthetic solutions (Figures (7.5), (8.1) and (8.2)). The intermediate figure gives the overall analyses of dried samples from a run on wood in a solution of pH = 5.4 to 5.7 (ca. 24°C) containing Fe^{2+}, $BaSO_4$, minor NaCl, HCl and glucose. The progress of the analyses (over one week) show the gradual loss of sulphur from solution, and the consequential relative build up of $BaCl_2$. The Ba peak is that at about 4.5 on the scale shown, Cl is at 2.6 and S is at 2.3 units. The corresponding analyses are given in Table (A.17), and are samples 5, 8 and 10. The iron sulphide produced is depicted in Figure (7.5). The major difference is that the cultured sulphide is slightly coarser grained than usual.

Concomittant with the iron sulphide deposition are many other insoluble sulphides which are able to form in the environment. The field pseudomorphs contain ca. 1000 ppm of mercury (Tables (A.4) and (A.6)). During changes in streams most of the pseudomorphs are inevitably exposed and corrode leaving cinnabar-rich sediments (Figures (7.6) and (7.7)).

In summary the reactions occurring in the formation of cinnabar concentrates from pseudomorphs (and probably other sulphides) are:-

1. Sulphate enters the stream from hot baths and/or oxidation of H_2S percolating through the stream.

2. Mercury enters the stream as Hg^0 or Hg II via hot bath over-flows and gas percolation.

3. Iron as Fe II enters the stream via ground-water seepages.

4. Mercury is oxidized (possibly before entering the stream).

5. Sulphate is reduced by the bacteria to sulphide.

6. Iron, mercury, copper and other trace metals produce their sulphides with the sulphide released on the outside of the bacteria.

7. Oxidative changes to the environment lead to the loss of nearly all the metal sulphides but cinnabar, which is relatively inert to acid-oxidizing conditions.

Of all the economically viable cinnabar which has been in the Tuwhakino area, about 65% was probably produced via the above mechanism. Virtually all the richest cinnabar deposits (e.g. the crusts in Bell and Clarke (1909) and Henderson (1944)) were in stream sediments. Hence the above mechanism is the most efficient of the ore deposition mechanisms operating at Ngawha Springs.

CHAPTER NINE MERCURY DISTRIBUTION

(9.1) SOILS

Correlations for significant variations of mercury concentrations in soils are given in Figures (9.1) to (9.5) which give a general impression of the results displayed in Tables (A.1), (A.3) and (A.10). Summarily organic materials (peat and top-soil) contain more mercury than montmorillonitic soils which contain more mercury than kaolinitic soils for a given situation. The relationship is grossly overshadowed by the proximity to, and the magnitude of mercury exhalations: Figures (9.3) and (9.4) depict the relationships for elemental and total mercury content in soils, cf. Figure (4.1). Figure (9.3) clearly delineates the known zones of high mercury concentrations and geothermal activity, and it shows up some minor new zones.

Of all the mercury species, the element appears to be the least dependent on soil-type and chemistry. The halo of anomalously high elemental mercury occupies about 5 km^2 (0.005 ppm is taken as the background level of total volatile mercury in the local soil).

a. The 'Montmorillonite' Soils

The background total mercury levels in the soils range from 0.017 to 0.065 ppm within the basin and may be as low as 0.01 ppm outside the basin. Where basalt (the parent-rock) is close to the major thermal emanations of zone 2 there is considerable variation in the total mercury content. It ranges from about 0.06 ppm to over 0.25 ppm (Tables (A.1) and (A.9)).

Basalt adjacent other areas of thermal emissions usually contains little more than background concentrations of mercury, commonly no more than 0.020 ppm of total mercury. The basalt along southern side of the upper Tuwhakino Stream area has the highest mercury concentrations, 0.23 to 0.28 ppm total mercury, but near the waterfall at N15/377350 the same basalt mass contains less than 0.1 ppm total mercury.

Most soil over basalt(s) steadily decreases in mercury content with depth (Figure (9.6)), unlike the trend for the other soils. The top-soil contains the highest concentrations of mercury which is generally two to five times the mercury concentration of the parent-rock. The greatest fall-off in mercury usually occurs between deposition horizon (B_2 montmorillonite-rich) and the fresh rock (D). The organic mercury trend (profile Q in Table (A.10) indicates that the organic mercury is strong-

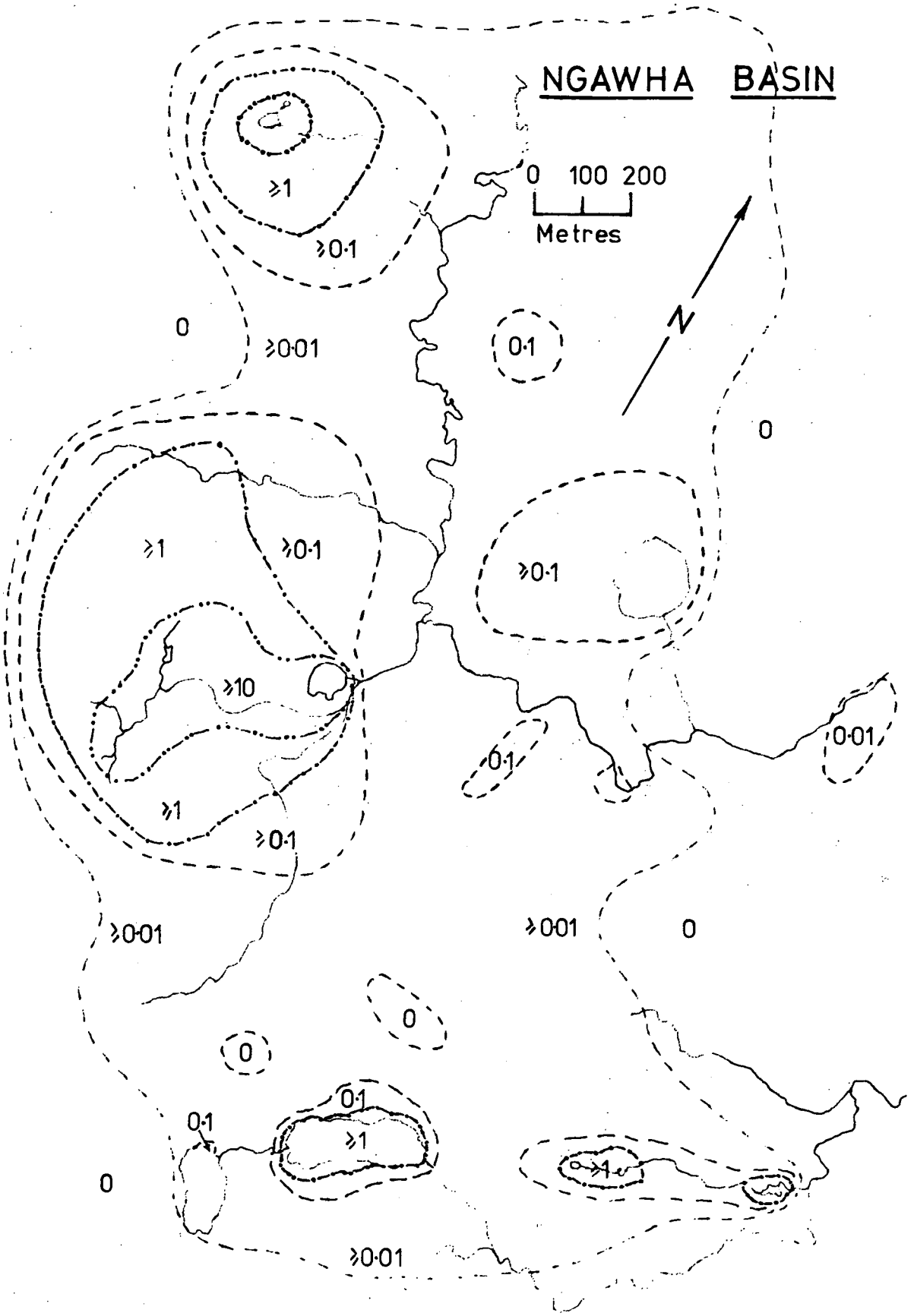


Figure (9.1) Total Mercury in Top-Soil (ppm)

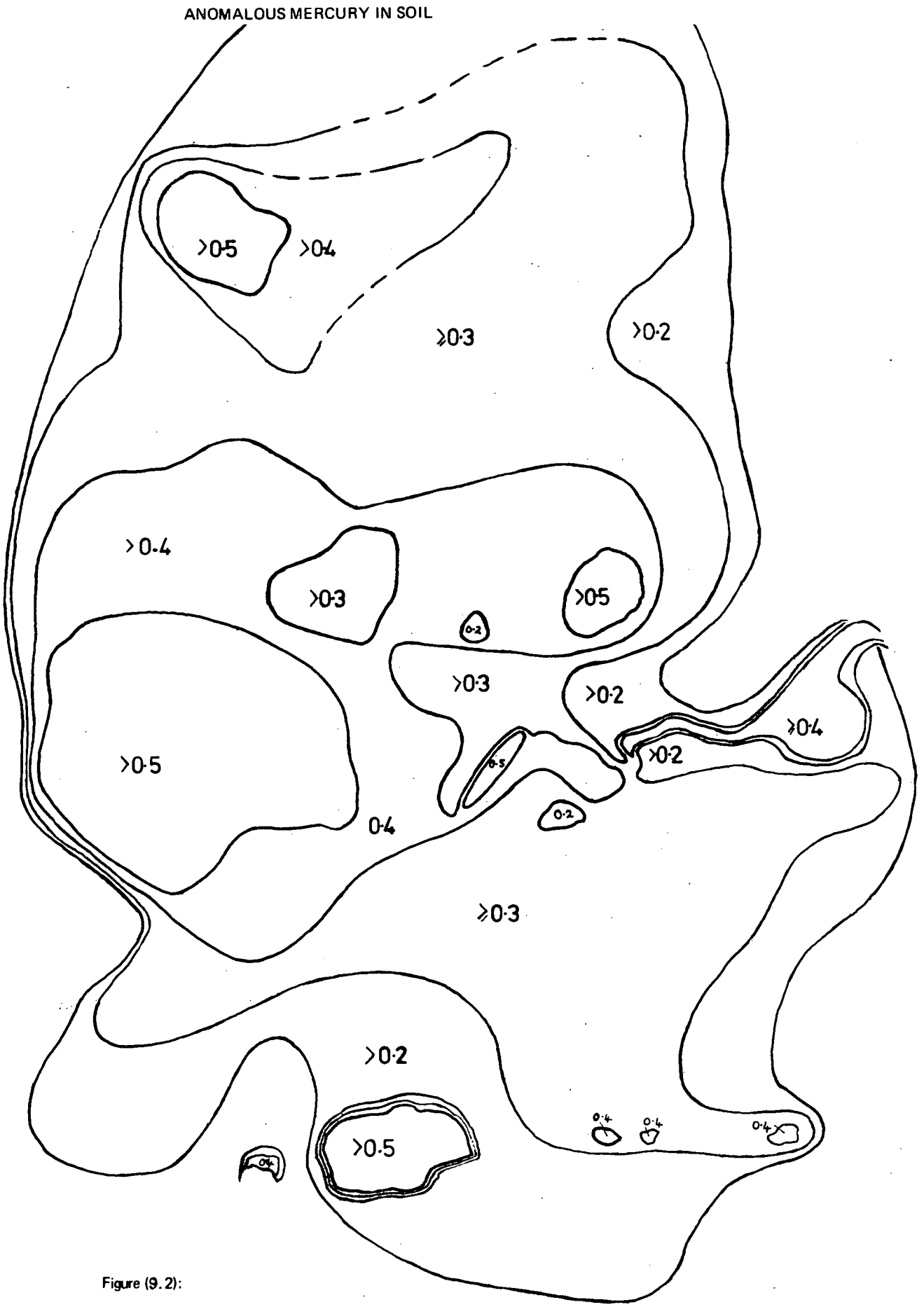


Figure (9.2):

Anomalous mercury in The Top-Soil of The Ngawha Basin (ppm)

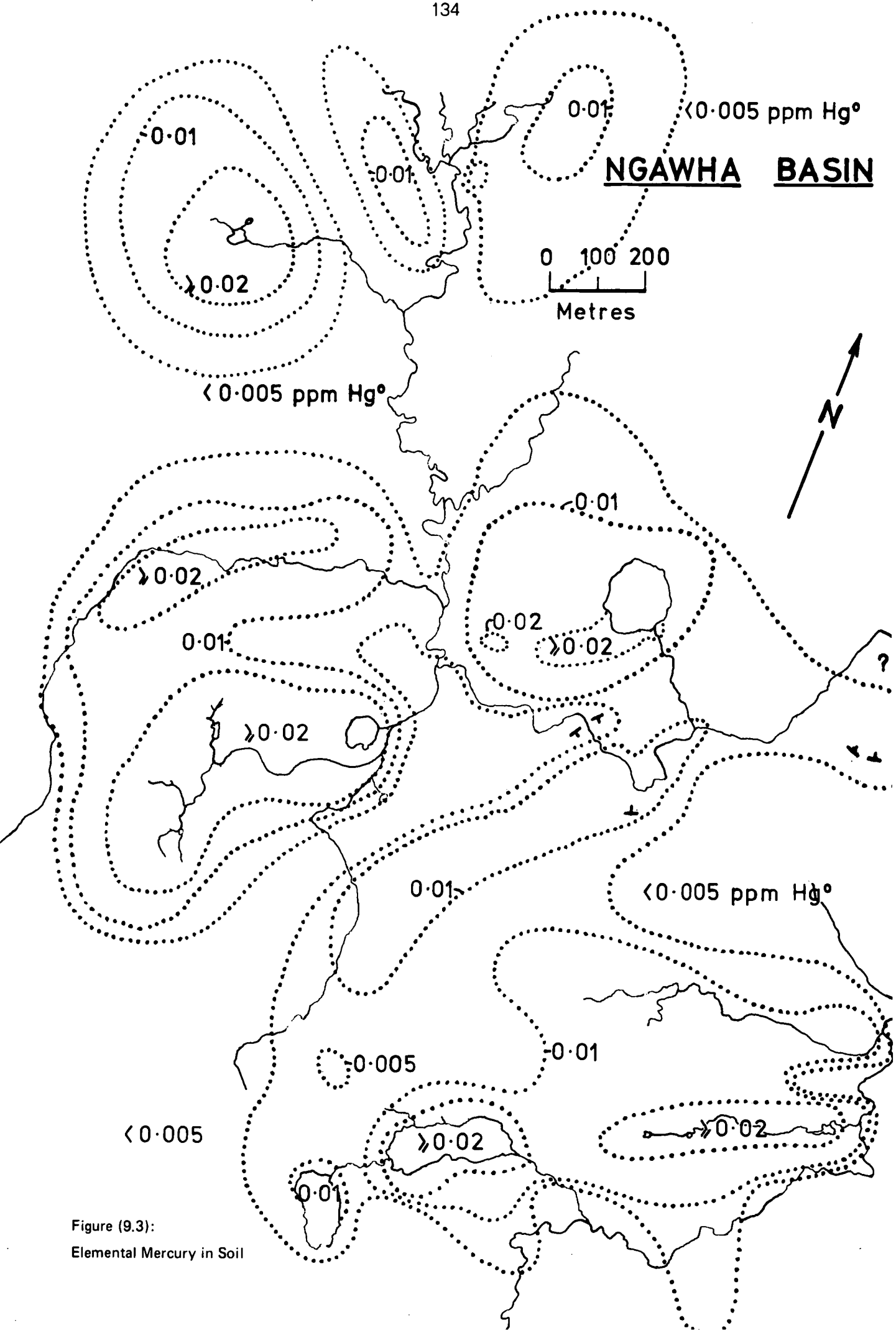
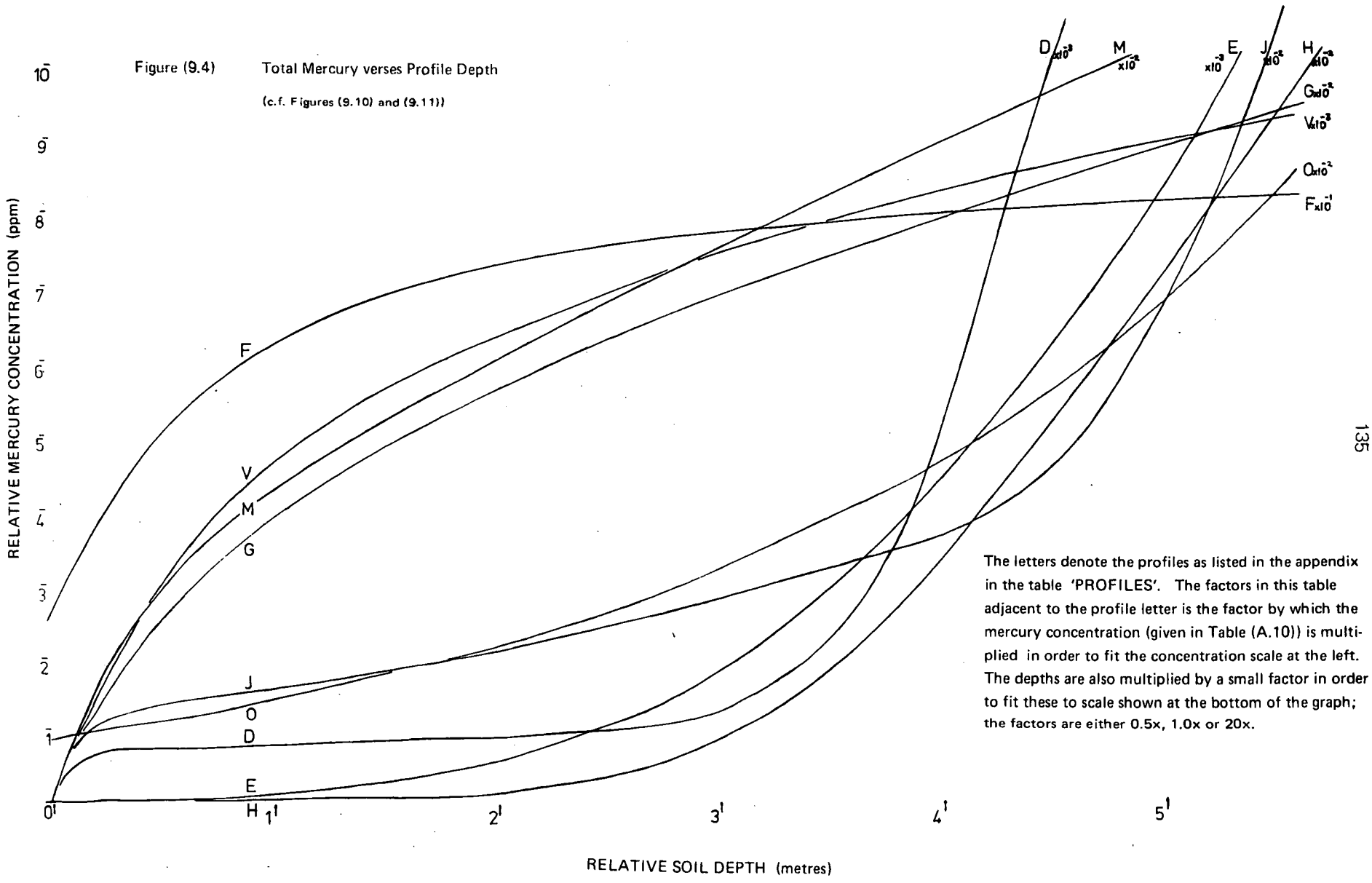


Figure (9.3):
Elemental Mercury in Soil

Figure (9.4) Total Mercury verses Profile Depth

(c.f. Figures (9.10) and (9.11))



The letters denote the profiles as listed in the appendix in the table 'PROFILES'. The factors in this table adjacent to the profile letter is the factor by which the mercury concentration (given in Table (A.10)) is multiplied in order to fit the concentration scale at the left. The depths are also multiplied by a small factor in order to fit these to scale shown at the bottom of the graph; the factors are either 0.5x, 1.0x or 20x.

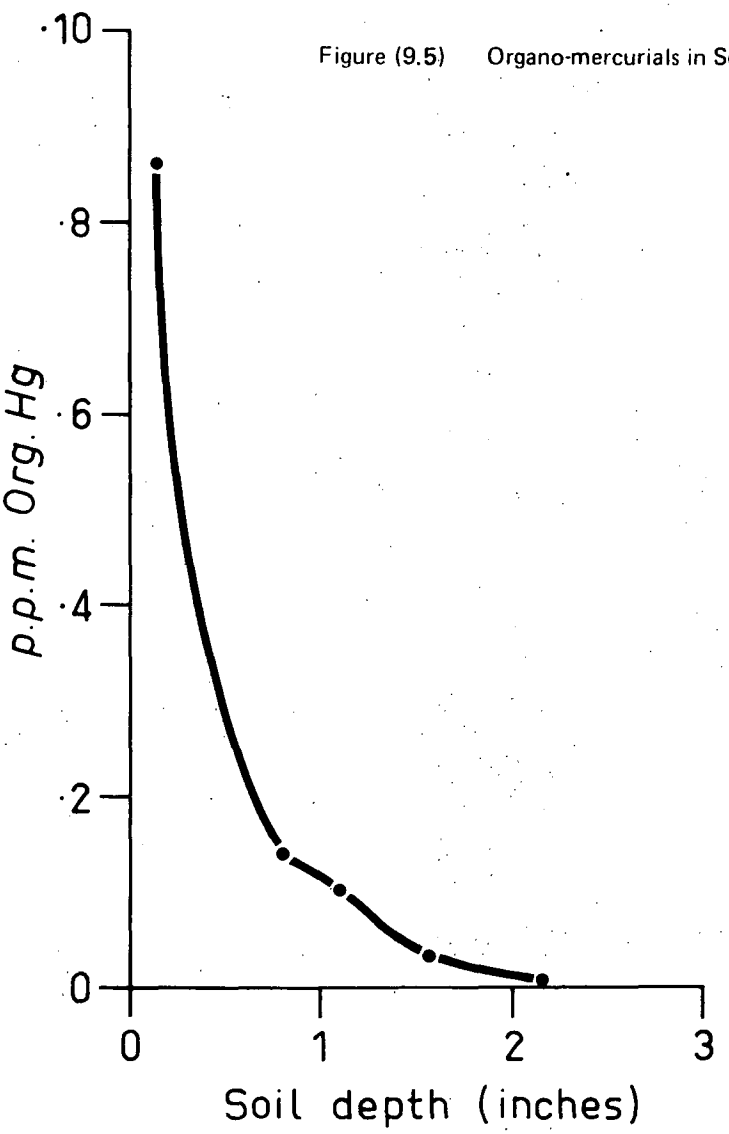


Figure (9.5) Organo-mercurials in Soil

ly associated with the organic material. It is highest in the organic and litter layers and falls to undetectable in the layers below. (In profiles near thermal activity the organic mercury is also high where any peat is present).

Near thermal emissions basalts soils commonly show a relatively lower mercury content than that expected by comparison with the other soil types of similar disposition. As noted earlier thermal emissions abruptly cease where they abutt basalt flows. No geothermal emissions have been observed where basalt is known to underlie an area, e.g. parts of the lower Tuwhakino Stream. Background levels of mercury in profiles may be reached as little as 20 metres in from the edge of a basalt mass, e.g. to the north-east of the Lower Sulphur Pool. Generally large falls in mercury concentration occur within a few metres of the basalt perimeter, with the exception of soils overlying deeply buried basalt. Hence basalt is relatively restrictive to the movement of mercury compared to the other superficial bed rocks, and this is reflected by the mercury analyses for both the rock and its overlying soil.

Apparently mercury is more able to penetrate the rock where temperatures are relatively high; e.g. above 50° the parts of the basalt mass close to hot spring activity along the central thermal strip have mercury concentrations of almost 0.3 ppm about 25 m inside the basalt mass.

b. The Chaos Breccia

Although the Chaos Breccia underlies much of the Ngawha Basin the soil formed from it is mostly outside or peripheral to the basin. Consequently anomalously high mercury soils over the breccia are rarely encountered. The main anomalies are at the extreme western ends of all three thermal zones and the eastern end of the central thermal strip. The chaos breccia has the highest background mercury of all the country rocks; the soils range in mercury content from about 0.015 ppm to about 0.65 ppm total mercury. The measured soil anomalies range from 0 to about 0.35 ppm total mercury and correlate with distance to thermal activity (Figure (9.1)).

The fall in total anomalous mercury content with increasing distance to the nearest area of geothermal activity may be relatively rapid (Figure (9.2)). This is very pronounced at the western end of the central thermal strip where background levels are reached within 150 metres.

Although topsoil development is usually poor, the organic horizons hold the greatest concentrations of mercury with rare exceptions. The mercury concentrations of the organic layers are similar to those over basalt and lake sediments. Unlike montmorillonite, kaolinite apparently takes up very little mercury, hence there is a promin-

ent mercury minimum in nearly all the chaos breccia profiles analysed (depicted in Figure (9.6)). Background mercury levels for kaolinite are about 0.05 to 0.08 ppm total mercury, and the basin levels do not appreciably exceed this unless there are mercury emanations close by (ca. $\leqslant$ 100 m).

The partially weathered and the fresh chaos breccia can contain appreciable amounts of anomalous mercury even though little might be taken up by the leached and deposition horizons. A few analyses of the relatively fresh breccia close to the Upper Tuwhakino area and to the north-west of it suggest a small increase in mercury content with depth, (which is probably related to geothermal mercury). The percentage of elemental mercury in the total mercury also tends to increase with depth in the bed-rock near anomalous mercury occurrences.

c. The Lake Sediments

The sediments are very porous unlike the basalt and the chaos breccia. Hence the lake sediment profiles tend to reflect what they overlie where they are thin. The high quartz content causes slow weathering and hence the soil is relatively shallow and not always well developed. Except for organic layers O, A_o and possible peat, horizons contain conspicuous quartz sand and silt; otherwise the profile sequence is similar to that of the chaos breccia (which is the main source of the lake sediments). Poorly drained areas have lowland acid peat profiles.

No thermal activity occurs outside the area of lake sediments, although in some instances recent erosion has removed most of the sediments. All the economic cinnabar and mercury are associated with the sediments, which gives rise to the largest range of mercury concentrations in any of the soils. The geothermal activity has disrupted and altered the nature of many of the profiles, hence these anomalous lake sediments profiles are treated separately as 'Geothermal Sediments' in a following section. The background level of mercury is lowest in the lake sediments compared with the basalt and chaos breccia. The background is about 0.005 to 0.008 ppm total mercury which allows anomalous mercury concentrations to be readily detected. High mercury levels pervade much of the basin, and from a given thermal area persist for over 0.2 km, but rarely beyond 0.5 km (Figure (9.3)). Where the sediments are thick and lie very close to thermal activity, the mercury content is highest and spreads over a wide area, and where the sediments thin a fall in mercury content usually results (compare Figure (9.3) and (4.1)). The fall-off in mercury content is even more marked where the sediments pass over basalt. The data given in Table (A.3) and depicted in Figure (9.3) indicate that wherever the lake sediments are thin (less than about 2.5 metres) that

the elemental mercury content also falls off most rapidly; e.g. near the perimeter of the sediments and where other facies penetrate into the soil horizons (solum).

d. Peat Soils

Peat soils have similar trends for mercury species as those previously discussed and behaves most similarly to top-soil. There is a strong correlation between organic content and organomercurial concentration, an inverse correlation between distance and total mercury concentration and a general eclipsing of mercury by basalt. The striking difference is the high proportion of elemental to total mercury (Table (5.10)). Near thermally active areas as much as 90% of the mercury present is the element. In one case profile (G) a smear of mercury was picked up on the author's hands. The profiles F, G and R are peat profiles: R is relatively distant from thermal influences, whereas F and G are respectively closer.

(9.2) BROAD SUMMARY OF MERCURY TRENDS

The above observations indicate that the lateral spread of mercury from a thermal source into the lake sediments depends on the thickness of the sediments. This in turn implies that mercury mobility is relatively inhibited by the other underlying materials, particularly basalt. Hence the series for mercury mobility in the Ngawha Basin is: lake sediments > chaos breccia > basalt.

The profiles they show that the total mercury content of soil correlates strongly with the organic content and weakly correlates with the inverse of the kaolin content. Regardless of the kaolin content some profiles within half a kilometre of thermal activity pass through a minimum total mercury content in the deposition or weathered rock horizons; the elemental mercury content commonly increases monotonically with depth (unless basalt underlays the area) (Tables (A.2) and (A.10)), and it is probably due to the increase in elemental mercury that the profiles show the gradual increase in total mercury with depth.

Results show that an undisturbed profile near thermal emanations e.g. profiles H, M and N in Table (A.10) has a rapid decrease in organic mercury with depth (Figure (9.5)), and increases in elemental, cold extractable and total mercury concentration. The elemental and cold extractable Hg concentration usually show a monotonic increase with depth, but the total mercury concentration may increase erratically. Where large increases in total mercury occur, it is usually below the soil-base; i.e. within the parent-rock.

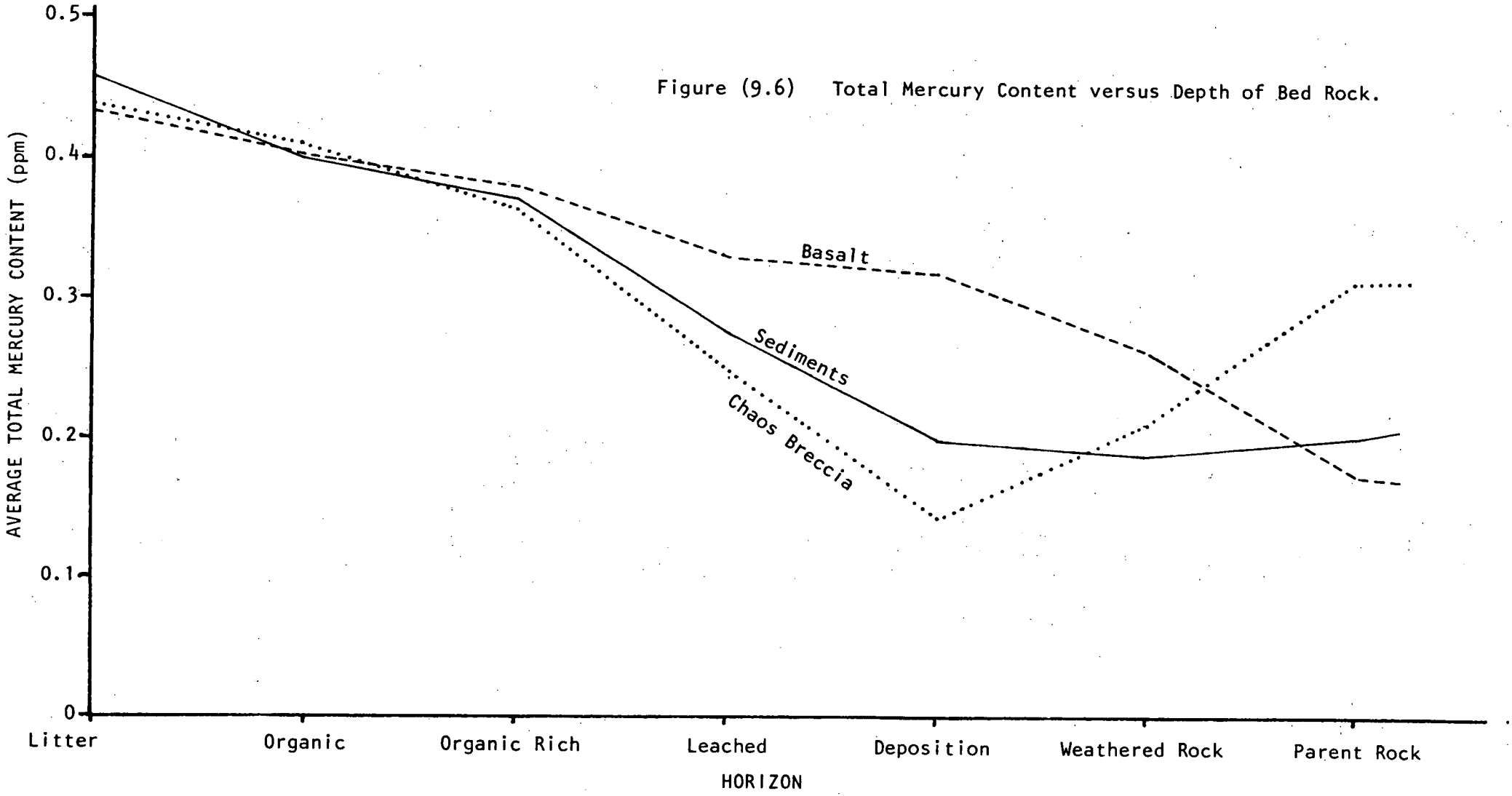


Figure (9.6) Total Mercury Content versus Depth of Bed Rock.

TABLE (9.1) Total Anomalous Mercury in Soil and Underlying Rock.

Classification	Area km^2	Gradient °C/km	Depth (to 215°) m	Anomaly ppm	Mass tonnes
Distal Soil < .1ppm	2.5)				
	)	-	1.5	0.040	0.52
Distal Soil > .1ppm	0.7)				
Distal rock (unembayed margin)	4.1	500	400	0.031	137.3
Proximal soil < 1ppm	1.4	-	1.6	0.265	1.60
Proximal soil > 1ppm	0.081	-	2	5.0	2.19
Proximal rock	1.54)				
	)	340	600	0.17	257.5
Source 'Country rock'	0.11)				

The total anomalous mercury in Ngawha soil is 4.31 tonnes.
The total anomalous mercury in unaltered rock is 394.8 tonnes.
Therefore the total mercury anomaly is 399 tonnes $\simeq$ 400 tonnes.

(9.3) GEOTHERMAL SEDIMENTS

These have many variations in composition as discussed in Chapter 4 and depicted in Figure (4.3). Essentially the sediments consist of the lake sediments and their soils, peat, hydrothermal minerals, vegetation debris, and minor amounts of weathering products from the chaos breccia and the basalts. Peat content usually increases with depth and a layer of vegetation debris and peat lie at the base of nearly all geothermally disturbed profiles except by large fumarolic vents where virtually all superficial material has been removed. Commonly only the surface few metres constitute the (reworked or) geothermal sediments.

It is in the reworked sediments for as much as 10 metres depth and 15 metres radius about the ebullient fumaroles that the major portion of all anomalous mercury lies. Profiles A, B, D, E, J, L, O, S, U and V of Table (A.10) represent the wide range of the geothermal sediments. Most of the major fumaroles lie in the Tuwhakino area (Figure (9.7) and Tables (A.15 and (A.18)), one is at Waiparaheke Pond and the remaining few are at Waitotera Pond. Below the geothermal sediments the total mercury content commonly falls off rapidly and the proportion of elemental mercury increases. (The mercury concentration in the rocks below the geothermal sediments is still considerably higher than background levels and is considered later.

The mercury held in the geothermal sediments is calculated by multiplying the respective area, average mercury concentration and depth, then summing the products. It should be noted that all large pools in the basin are geothermal in nature and hence the sediments are geothermal sediments. A brief discussion of pool and stream sediments is given in the following section, however for completeness all thermal components are included in Table (A.18), 'Total Mercury in Geothermal Sediments.'

(9.4) AQUEOUS SEDIMENTS

a. Pool Sediments

All pools are or have been thermally active, and the sediments contain abundant anomalous mercury (Table (A.7)). Mercury concentrations in contemporary sediments vary according to current gas output and temperature. Gas-flow correlates more closely with concentration where temperature exceeds 25°, but below 25° other influences commonly disturb the relationship, particularly the influx of fresh meteoric water. Where the gas-flow is less than about half a litre per minute, temperature usually shows a better correlation than gas-flow: cf. Figures (A.8) and (3.8) and Table (A.16).

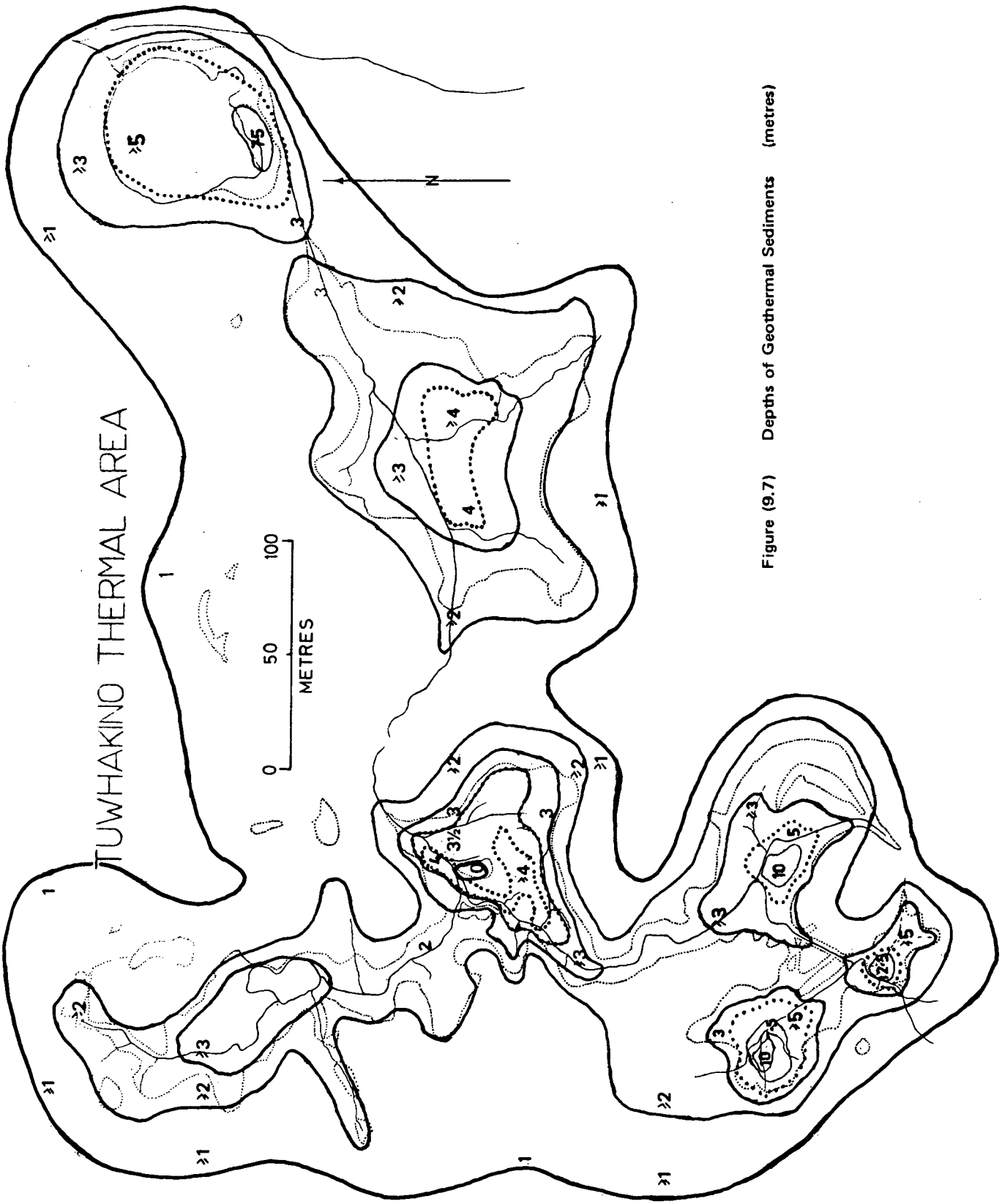


Figure (9.7) Depths of Geothermal Sediments (metres)

The pool sediments consist of the previously mentioned 'geothermal sediments', stream sediments, colloidal sulphur, limonite, organic material and clays. On the colloids appreciable mercury may be adsorbed. Detrital cinnabar also may be present in the Tuwhakino and Waitotera areas. The total mercury in the pool sediments is about 2.5 of the 70 tonnes per Table (A.18).

b. Stream Sediments

A brief survey of stream sediments along the Ngawha Stream to the sea near Waitangi shows that the mercury concentration in the minus 85-mesh fraction decreased almost exponentially with distance from the basin (Table (A.7) and Figure (9.8)). There is a noticeable negative deviation from the exponential decrease between the large (N15/383358) and small (378350) land slips. This is probably due to a considerable influx of material recently. Significant decreases in mercury concentrations also occur after the confluence of the Manaia Stream and the Waiaruhe River, and from the confluence of the Waitangi and Waiaruhe Rivers.

A few kilometres from the confluence with the Waitangi River, and about 25 km from the Ngawha Basin, near background mercury concentrations are reached in the sediments and waters of the river in spite of agricultural pollution. Below 33 km there is an appreciable increase in water use and domestic effluent. The Waitangi River becomes estuarine at the base of the Haruru Falls (41 km) and suffers an abrupt change in chemical environment, but this is not particularly marked by the mercury analyses (Table (A.7)). Above and below the falls mercury concetrations are similar, possibly because the increase in salinity simply causes the flocculation of the suspended matter contained in the freshwater, which gives rise to fine-grained sediments similar to those above the falls.

The results in Table (A.7) indicate that there is probably no other comparable source of anomalous mercury in the watershed of the Waitangi River. No tributary of the watercourse analysed has a significantly larger flow than the lower Waiaruhe River, hence sufficient dilution of a comparable mercury anomaly is unlikely. No other tributary exceeds the length of the one studied, nor are there massive land-slips which may introduce large quantities of adsorbing material (as are along the Ngawha Stream). Hence complete distribution of mercury due to distance is unlikely, because the discussed adsorption capacity would increase the magnitude of the down stream anomaly.

(9.5) PRIMARY MERCURY DISTRIBUTION IN SOIL AND ROCK

Broad-scale mercury concentrations can be correlated with distance to the nearest mercury emission(s). However the overall correlation is best treated by division into a series of vertical and horizontal (radial) distributions which depend on the dis-

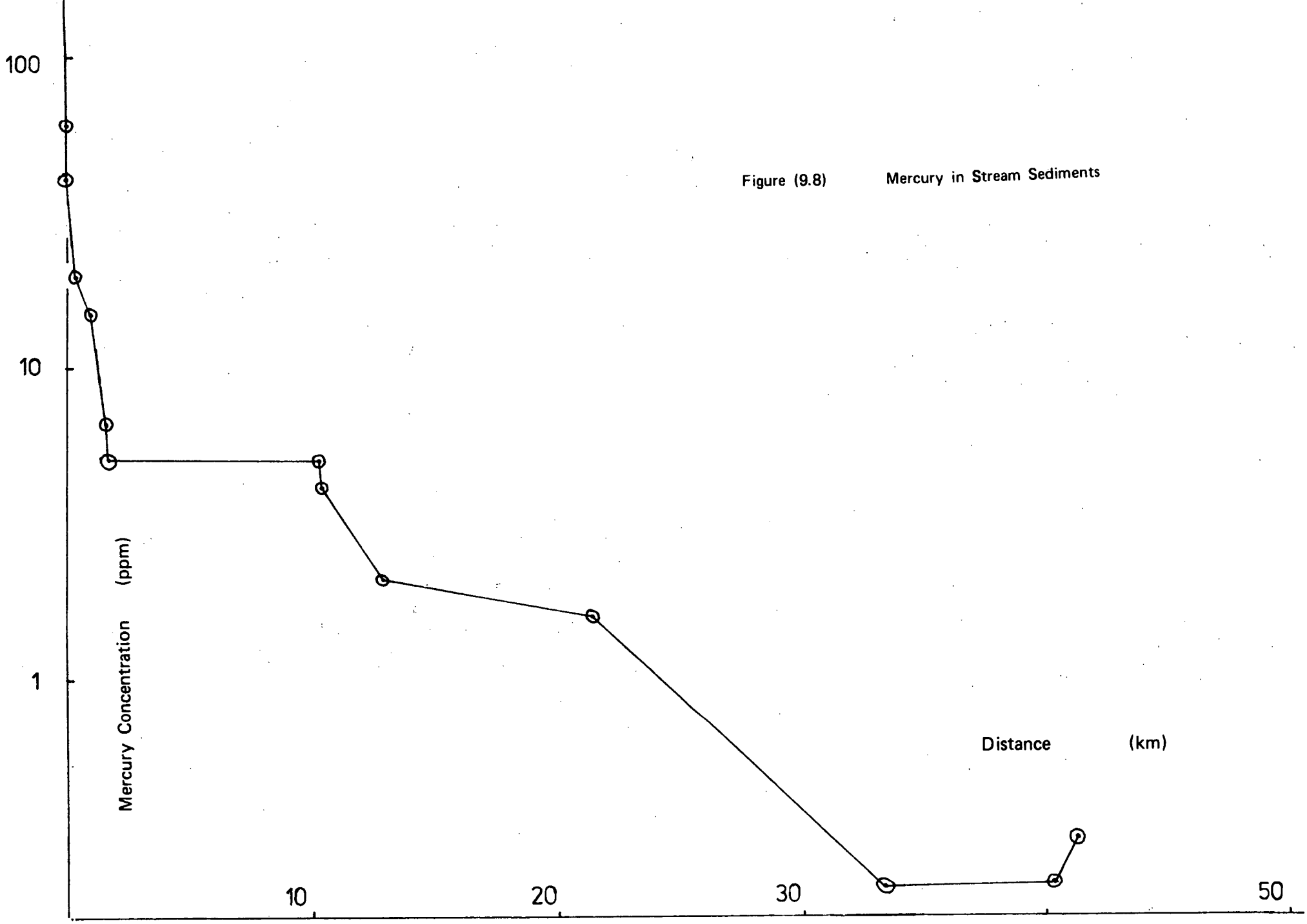


Figure (9.8) Mercury in Stream Sediments

a. Horizontal Mercury Distribution

Outside the geothermal depressions, the lateral variation of total anomalous mercury with distance to the closest centre of thermal activity is fairly regular within any given rock or soil horizon. Within the large geothermally active depressions the variation is commonly erratic. The regular relationship is an exponential concentration decrease for increasing distance, and is most obvious for directions away from all thermal activity in the basin; e.g. Figure (9.9) is for the chaos breccia south-west of Waima.

The empirical equation denoting the change in mercury concentration with distance is:-

$$\ln [\Sigma Hg] = \frac{A}{d + B} + C \qquad A, B > 0; C < 0 \text{ and } \frac{A}{B} \gg |C|.$$

A, B and C are constants which depend on rock-type, direction and mercury concentration, d is the distance to the nearest major fumarole of high mercury content, exp C is the background mercury concentration, and exp $(\frac{A}{B} + C)$ is the maximum mercury concentration at the fumarole. (B is a measure of the attenuation of the mercury concentration and hence reflects the geological medium: The smaller B, the more rapid is the fall-off in mercury concentration with distance. A reflects the maximum mercury concentration(s) present).

Complications are caused by changes in geological environment, depth and the presence of several centres of major mercury emissions close together. Nevertheless mercury concentrations decrease with increasing distance from emanations. The lateral distribution can be directional: A, B and C may change according to geology and background mercury concentration, even though $(\frac{A}{B} + C)$ remains constant for a given centre.

The radial distribution of mercury about thermally active centres demonstrates that the only major source for the anomalous mercury is the zones of high mercury emissions, and that mercury is able to move through the ground.

b. Vertical Mercury Distribution

There are three groups of correlations for depth verses mercury concentration in soils (and shallow rock) which are characterised by the lateral distance from thermal activity. The correlations are thus classified as distal, proximal and deposition zone trends, and the areas containing them are thus named:

i The Distal Zone

ii The Proximal Zone and

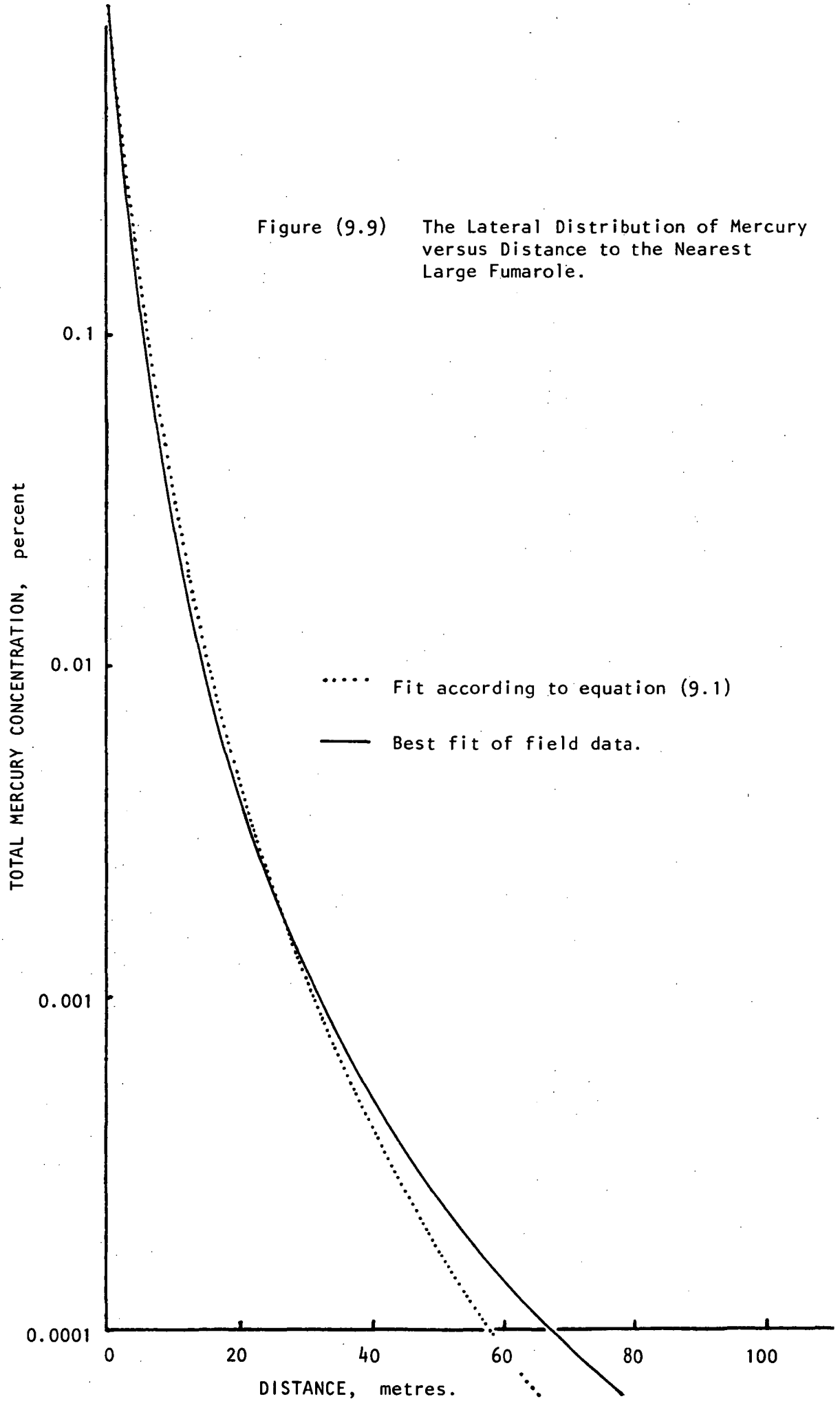


Figure (9.9) The Lateral Distribution of Mercury versus Distance to the Nearest Large Fumarole.

iii The Deposition Zone

Examples of i and ii are depicted in Figure (9.4), and examples of iii are in Table (A.10).

b.i. The Distal Zone

All areas more than about 60 m from an area of mercury emanation(s) are distal. In areas of very low thermal activity (e.g. Sulphur Ponds) the distal classification may apply from 25 m. The characteristic of the distal classification is the convex (upwards) plot of total anomalous mercury concentration verses depth for the soil and superficial country rock: i.e. the rate of increase of anomalous mercury concentration decreases to a constant or a linear trend. Tables (A.10) and Figure (9.10) and (9.4) respectively give typical data and trends.

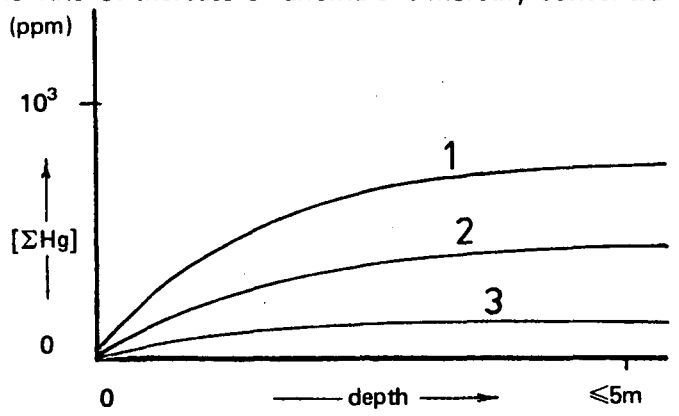


Figure (9.10) The Distal Mercury Trend

Once the chaos breccia or basalt is encountered there is usually a change to a constant concentration of total anomalous mercury. Superficial basalt commonly blocks the anomalous mercury, causing near background levels of mercury.

Figure (9.10) indicates the usual range of trends in any direction which passes through a centre of geothermal activity. The numbers in increasing order represent profiles at increasing distances from the geothermal centre. Profile number three (which rapidly tends to constant anomalous mercury) is usually encountered by about 100 m from thermal activity (e.g. F in Table (A.10)). At 100 m the maximum total mercury concentrations are less than 10 ppm. Analyses of samples from bores and deep gouges indicate that at least to depths of 100 - 150 m little or no change in total anomalous mercury concentration occurs beyond that found at 2 - 3 m depth.

The other two profile trends shown in Figure (9.10) also become constant with depth, usually after entering the chaos breccia. (Near the interface of the lake sediments and the chaos breccia the mercury concentration falls most rapidly; e.g. 15 m west of the Tiger Bath). The constant mercury anomaly at depth for trends 1 and 2 is respectively higher than that for profiles like number three.

The quantity of anomalous mercury contained in the superficial material and the underlying country rock is calculated in Table (9.1).

b.ii The Proximal Zone

Within 60 m of thermally active areas (excluding the active ground) lies the proximal zone. It is characterised by concave (upwards) plots of total anomalous mercury concentration verses depth. Plots for some profiles appear in Figure (9.4) which shows the initial rate increase of mercury concentration to depths of about 3 - 5 m. The rate of increase in mercury concentration is about constant for up to a few metres then by depths of 5 - 8 metres it has become negative (Figure (9.11). It is near the water-table surface and no more than one metre below it that the total mercury concentration usually reaches the maximum. The numbers on the curves in the figure are in order of increasing distance from thermal activity, and indicate that the nearer a site is to thermal activity, the greater the rate of increase in mercury concentration with depth. (Parallelling this gas activity broke out in many profiles close to thermal activity, also a few profiles had visible cinnabar near the water-table).

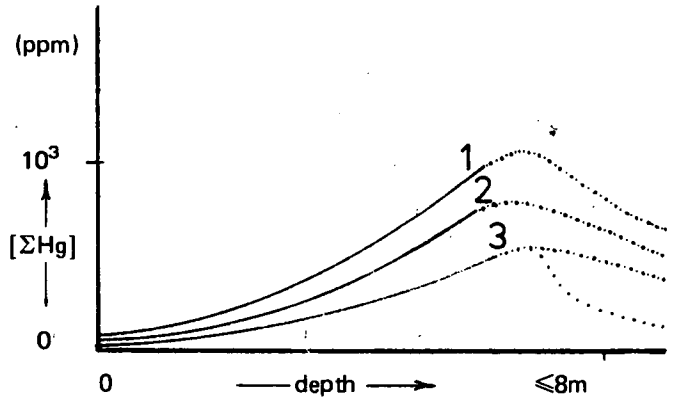


Figure (9.11) The Proximal Mercury Trend

The many thousands of bore-holes sunk by mining companies gave similar trends for bore-depths ranging from six to over sixty metres (Griffiths, 1898; Bell and Clarke, 1909 and Henderson, 1944). The ratio of total mercury to elemental mercury also peaks at the water-table or just below Figure (9.12). The mercury concentrations range from ca. 100 - 5000 ppm maxima to less than 15 ppm by 10 m depth. The several recent shallow drill-holes (1976) to depths of 40 - 110 m indicate that very similar abundances of mercury (0.3 - 12 ppm) persist deeper (Table (A.21)). The lowest concentrations (0.2 - 0.5 ppm) were found in unaltered basalt as close as 40 m from hot geothermal upwellings.

b.iii. The Deposition Zone Anomaly

The zone contains the highest concentrations of mercury. In the upper three metres the concentration very commonly exceeds 100 ppm and has an erratic distribution (Table (A.15) and Figures (9.7) and (A.12)). Below this the 'ore-horizon', the mercury concentration strongly decreases with depth, although high mercury concen-

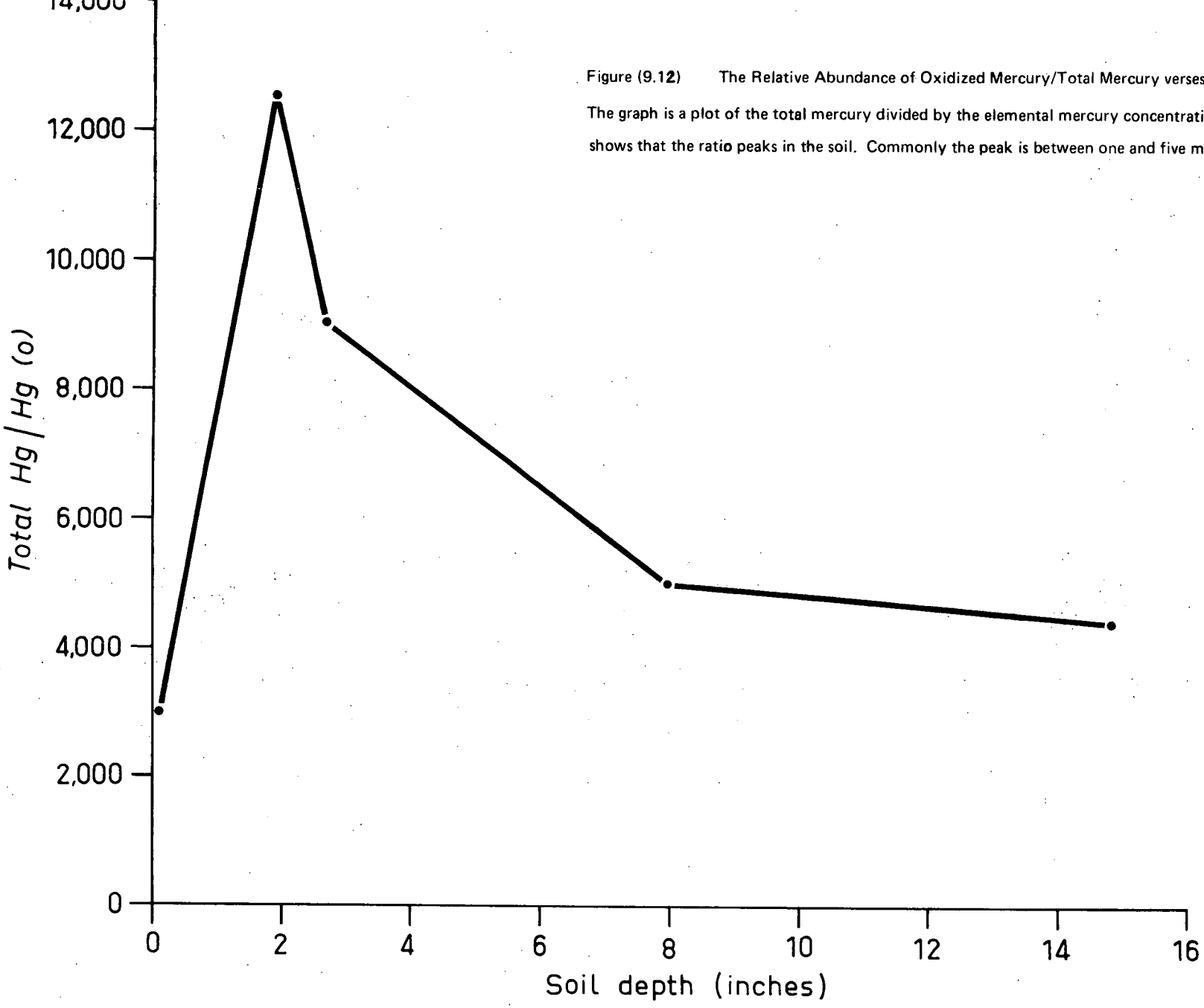


Figure (9.12) The Relative Abundance of Oxidized Mercury/Total Mercury verses Depth. The graph is a plot of the total mercury divided by the elemental mercury concentrations, and shows that the ratio peaks in the soil. Commonly the peak is between one and five metres depth.

trations follow most fumarole feeders. Below 15 to 20 m mercury is almost uniformly distributed with the highest concentrations (10 to 50 ppm) centred on the hydrothermal plumbing.

For easy calculation of the total mass of anomalous mercury present in the cinnabar depositing areas, the deposition zone has been divided into five regions per figure (9.13).

i. Geothermal Sediments,
ii. Ore Shoots,
iii. Non-ore-grade Cones,
iv. Vent Walls,
v. Country Rock and
vi. Mined Mercury.

The sixth member of the list is not a region but is necessarily included to account for mercury which was present in the five regions prior to mining.

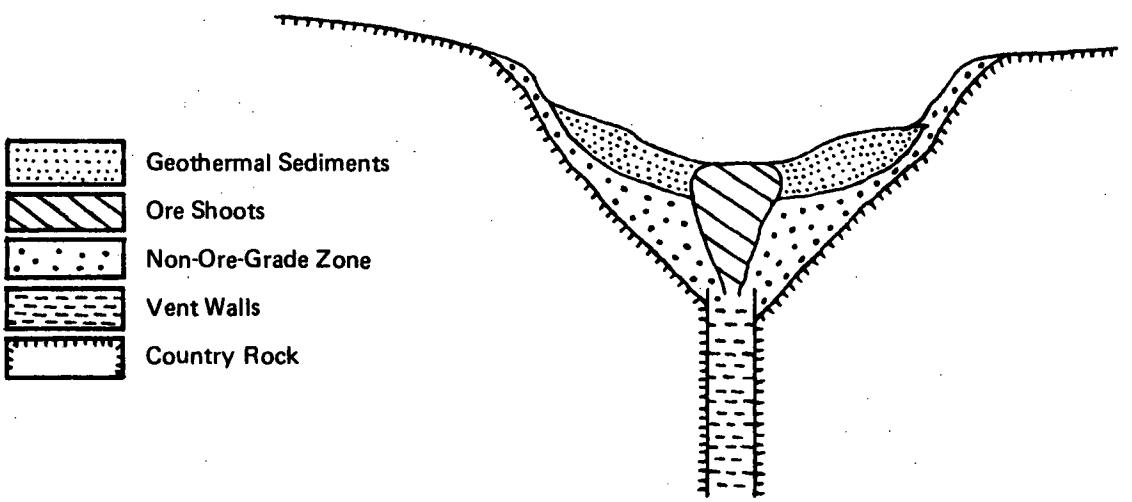


Figure (9.13) Geothermal Sediments

(9.6) THE DEPOSITION ZONE

a.i. Geothermal Sediments

The geothermal sediments which were discussed earlier in this chapter contain about 70 tonne of mercury, see also Table (A.18).

b.ii Ore Shoots

The ore shoots are the parsnip-shaped volumes rich in cinnabar centred around fumaroles to depths of about five metres. They have been mined out in most places, and the remnant has been included with the geothermal sediment calculations. Prior to 1895 the ore-shoots would have contained about 80 tonnes of mercury (in ore of $\geqslant$ 0.5% Hg).

c.iii Non-ore-grade Cones

Surrounding the ore-shoots is a larger parsnip or conical-shaped zone of sub-ore grade material which contains 65 tonnes of mercury per Table (9.2). The quantity is calculated by multiplying the average mercury concentration in each cone by the volume and the average ground density. Excepted from the cones are the volumes of high mercury concentration which follow the fumarole plumbing below the ore-shoots. Some of the relatively wide cones are slightly concave, however this does not introduce a significant error because the perimeters are lowest in mercury concentration.

d.iv Vent Walls

Continuing below the apices of the non-ore-grade cones are narrow zones of anomalously high mercury concentrations which follow the fumarole feeders. Because of the known uniformity of mercury distribution at depths below 15 to 20 m, (although in situ data below 110 m is scarce), it is assumed that a uniform concentration distribution continues to the hydrothermal convection system / reservoir at ca. 215° C, which is still in the chaos breccia below all the active centres. The relative impermeability of the chaos breccia to fluids means that the lateral movement of mercury is limited to diffusion, hence very high anomalies are expected (and found) to be only about the hydrothermal plumbing, and form a near cylindrical outline.

The cylinders are about 15 m in radius and have circumference mercury concentrations in the range 0.5 to 20 ppm and up to ca. 50 ppm in the centre. There are few bore-hole analyses outside the Tuwhakino area, so some calculations have been made by comparison of known data. However outside the best studied areas there is relatively little mercury, hence the two to three percent extra mercury could be neglected.

The Tuwhakino area which has about 8.3×10^4 square metres within 15 m of vents averages almost 8.5 ppm total mercury and has a thermal gradient of about 650° C / km. Hence the relevant ground volume is 2.5×10^7 m ^{2} and holds about 430

tonnes of mercury. Subtracting the overlap with the non-ore-grade zone leaves about 400 tonnes. For the Waitotera and Waiparaheke areas the masses present are 5.3 and 2.0 tonne respectively. The other areas contain much less mercury. Therefore the total anomalous mercury held in the vent walls is about 410 tonnes.

e.v Country Rock

The country rock is the remaining ground not covered by any of the above anomalies. Since it contains low concentrations of mercury, it has not been separated from the surrounding anomalous country rock and is included in Table (9.1) as part of the Proximal Rock.

f.vi Mined Mercury

Also part of the total mercury anomaly is the mercury taken away between 1884 and 1934. Unfortunately nearly all the primary records of the early prospectors and mining companies are lost, however sufficient description is available in the literature to make a close estimate of the amount of mercury taken.

The Kaikohe Development Company (1927 - 1934) took 18.5 tonne of mercury after a 70% recovery rate (Henderson, 1944): i.e. about 26 tonnes were mined. The other significant mining operation is described by Griffiths (1898), whose data allow calculation of the mercury processed and recovered. Under the conditions described during 1895 - 1897 about 50 tonnes of mercury in 1.5% Hg ore was smelted to yield about 35 tonnes of the liquid element.

Prior to 1895 only a few tonnes of cinnabar had been taken (Bell and Clarke, 1909). The two mining companies have taken most of the economic mercury: by about 1931 'ore' containing 0.002% Hg was being smelted (Henderson, 1944). Since 1934 no mining has taken place, and there was no mining of note between 1898 and 1927.

The lost mercury due to mining is therefore about 85 tonnes. This includes the flue losses which escaped to the atmosphere, and five to ten tonnes of mercury taken by minor mining and prospecting.

TABLE (9.2) Non-Ore-Grade Source Anomaly.

Location	Radius (m)	depth (m)	Volume ($m^3 x 10^{-5}$)	Concentration (ppm)	Mercury (tonnes)
Waitetera	60	35	1.32	20	4.6
Tiger	20	40	0.17	150	4.4
Waima	15	40	0.01	175	2.9
Flat	25	40	0.26	180	8.3
Pig	40	40	0.67	120	14.1
S. Pool	27½	30	0.23	45	1.9
Domain	50	40	1.05	75	13.7
Spa	45	35	0.74	70	9.1
Waiapawa	50	40	1.05	5	0.9
Waiparaheke	75	40	2.36	10	4.1
Ngamokaikai	20	30	0.13	5	0.1
Sulphur Ponds	15	30	0.07	15	0.2

The total mercury contained in the non-ore-grade is 64.3 tonnes.

(9.7) THE GEOCHEMICAL SOURCES

The possible sources for mercury (and most other hydrothermal species) are restricted to the geological environment which consists of soils, rocks and hydrothermal associations, however only the country rocks are a feasible source for mercury. All significant quantities of rock within a 20 km radius of Ngawha Springs have been considered as possibly related to the geothermal system. The use of quantities (volume and mass), stratigraphy, age, thermal gradient and spring and rock composition readily limits the possible major sources for geochemical components to two major deep sources and one shallow source. Similarly the energy may be supplied by one of two possible magmas.

Total analysis for some country rocks are given in Table (A.5), mercury abundances for the less significant rocks are presented in Table (A.9), and other related data appear in Tables (A.1), (A.4) and (A.10). In the context of this thesis it is mercury which is of most importance, and to a lesser extent some other chalcophile elements (Cu, Fe and Sb mainly). Based on these metals (and physical data) one can show all the pertinent relationships between the country rocks and the main physical and chemical processes in the thermal system: the identification of source materials, transport media, mobile species, host media, mechanisms of deposition, and flux depend on the analyses. Major element analyses proved to be of little use, probably because of their presence in all country rocks and their apparent lack of observable reaction and deposition. The very useful exception is iron because of its reaction with H_2S.

Each of the possibly contributing rocks or rock groups to the thermal system is discussed separately in the following text.

a. The Basement Group

The basement commences 400 to 600 m below the Ngawha Basin where the thermal gradient exceeds 350° C/km, thus the local basement temperatures exceed ca. 145°, and are known to reach at least 236° (Ellis and Mahon, 1966). Hence if there is any mercury in the basement components, the basement must be considered as a source for the geothermal mercury.

No core material was available from NG1 (600 m) however fluid escaping from the bore contained several parts per million free mercury. The nearest exposure of basement material (mostly pelitic siltstones) is 10 km east of Ngawha Springs and stratagraphically the same as that encountered below the Ngawha Basin (Skinner, 1966). The

argillite averages about 0.035 ppm total mercury, which is lower than the average for global argillites which is about 0.19 ppm total mercury, (in the range of 0.01 to 1.5 ppm Hg (Gatehouse, 1973). Greywacke is the other main constituent of the basement, but no fresh outcrops were found at sites visited near Ngawha. However samples were obtained near the coast to the east and south-east and these contained about 0.14 ppm total mercury.

It is probable that only the above mentioned two materials contained appreciable concentrations of mercury relative to the other materials which are minor components of the basement. Even if the other materials contain no mercury, there is more mercury in the uppermost kilometre of basement below the basin than in the whole mercury anomaly of the Ngawha Basin (Table (10.1)). As a minimum estimate, one cubic kilometre of basement material has at least 0.03 ppm mercury; i.e. contains a total of 100 tonne of mercury. Therefore below the unembayed basin floor alone a thickness of about 1 kilometre of basement would have originally held at least 1500 tonne of mercury.

No reports of significant organic material in the basement have yet been reported, however this does not rule it out as a possible origin for all or some of the hydrocarbons in the deep geothermal fluids.

b. The Chaos Breccia

The chaos breccia varies considerably from silicious or argillaceous shales to carbonaceous or calcareous argillites. Due to the common heterogeneity of the breccia whole rock analyses were only done on a few samples where the breccia was relatively uniform, however mercury was analysed in every sample obtained and varied from 0.014 to 0.65 ppm in bulk samples.

The whole rock analyses sample 3 in Table (A.5) is representative of the least weathered breccia samples to the west and north-west of Ngawha Springs (in particular N15/358345). There is over 90% SiO_2 which probably accounts for the local relative chemical stability to weathering. Here the total mercury concentration is lowest and ranges from about 0.01 to 0.03 ppm, and represents a background abundance. This is strongly supported by the fall-off in elemental mercury per Figure (9.3).

To the east, the closest exposures of breccia in the Ngawha Stream are calcareous (N15/378350), and they contain up to 35% calcium. Analyses are variable

in this weathered/altered rock, the total mercury ranges from 0.12 to 0.5 ppm. Downstream 1 to 1.5 kilometre the breccia is a deeply weathered pelitic shale and has 0.13 to 0.65 ppm total mercury, which are the highest non-anomalous abundances found. A number of mercury analyses are given in Table (A.1) under 'Rock' for soil profiles classified as type c.

The chaos breccia appears to directly overlie the basement (Skinner, 1966) hence it is probable that much of the lower portion of the chaos underlying the basin is hot enough to evolve mercury. Maximum expected temperatures in the central region by extrapolation of the geothermal gradient are about 275°C, and more than 5 km^3 of chaos breccia is at temperatures above 120°C. The average mercury content is over 0.3 ppm mercury; i.e. up to 4 x 10^3 tonne of mercury are available to the geothermal system. Hence the breccia can contribute significant amounts of mercury.

The main objection to the chaos breccia as a major dynamic source is that it has a low permeability to fluids (Healy, 1945 and 1972; Kear, 1966). Hence mercury evolution is hindered and strongly dependent on diffusion; so escape may be a slow process compared to that from the basement materials.

For a further background comparison of mercury in the relatively localised chaos breccia compositions, the limestone component at N15/378350 was sought from a non-thermally active and non-mineralised area. Two types of limestone may occur in the breccia: the Landon Limestone (Lower Oligocene) and the Opahi/Waimio Limestone (Middle Lower Eocene). The limestones were sampled at Tuhipa (6 km east-south-east), Pokapu (10 km south-east), Opahi (17 km south-east) Waimio (20 km east) and near Hukerenui (30 km south-east). Most of these limestones were generally less pelitic than the boulders at N15/378350. The Opahi Limestone showed the closest relationship and contained 0.03 to 0.06 ppm total mercury as compared to 0.025 to 0.07 for the one present in the chaos breccia. (The other limestones contained mercury in the lower part of the above concentration ranges and down to 0.014 ppm). Therefore the limestone found at N15/378350 contained close to background levels of mercury.

Since some areas of chaos breccia are reported to be carbonaceous (Healy, Skinner and Bowen, 1966; Blattner, 1978) and a coal (Middle to Upper Eocene) is known to have formed during the time interval represented by the chaos breccia, coal from Kawakawa was analysed (sample 2 in Table (A.5)). Gas emanating from the thermal area contains six to nine per cent hydrocarbons, condensates with traces of organo-mercurials and significant ammonia which suggests an origin such as coal or

petroleum (with degraded protein material) is very possible. Petroleum is unknown in the area. The Kawkawa coal contains significant traces of mercury (1 to 4.5 ppm), antimony (6 ppm) and selenium (3 ppm). Although the presence of coal may appreciably raise local mercury abundances in the breccia, the relative scarcity of coal in the breccia implies coal is a minor source of mercury when compared to the abundant shales and pelitic argillites.

Nevertheless the organic content of the chaos breccia may be sufficient to produce all of the evolved hydrocarbons (which are dominated by methane). The total amount of organic gas lost to the atmosphere averages about 5% of the gas evolution of 1250 l/min for the last 6,850 years; i.e. about 1.4×10^5 tonnes which as carbon in coal represents about a 40 metre cube. However the percentage of hydrocarbons pyrolised from coal varies from 10 to 40% w/w at one atmosphere (McKeown, 1953) and is higher at higher pressures. Therefore at least 15% volatile hydrocarbons are expected from the coal, that is a cube of about 80 metres length of coal is required. The Kawakawa coal measures are 15 metres thick (Kear and Hay, 1961) hence it is feasible that such a volume of coal could be present in the breccia. This is equivalent to about 35 ppm v/v, or 25 ppm w/w which is not particularly carbonaceous!

c. Basalt

The basalts are very late Tertiary and Quaternary, surface flows, hence basalt is unable to play a significant role in the production of geothermal components in the rising fluids, although the basalts are all cold except for the north-west edge of the flow bordering the central and upper Tuwhakino Stream, which is heated by rising geothermal fluids.

The total volume of basalt is relatively small, almost one cubic kilometre lies within the 200°/km isogradient which covers an area of about 1,500 km^2. The basin and adjacent environs contain about 0.5 km^3 of basalt with a maximum of 20 tonnes of mercury which could be evolved from the average 0.015 ppm total non-anomalous mercury: less mercury than that recovered by mining!

The basalts in the region of the basin differ little chemically and petrologically although there is more than one flow-type. The younger Taheke Basalts border the basin to the north whereas the older Horeke flows mostly lie below the lake sediments. Samples 1, 4 and 6 of Table (A.5) are the whole rock analyses. Table (A.9) gives total mercury analyses.

Sample 1 is very altered whereas 4 and 6 are fresh specimens. 4 is from the 106 metre bore near the Ngawha Springs Hotel, and 6 is from the waterfall area where analyses closely approximates those of basalt from 100 metres north-west of the Lowest Sulphur Pool. Sample 4 is typical of basalt near vigorous geothermal activity: commonly there is a marked increase in mercury, water, sulphur and other volatiles and a distinct decrease in antimony concentrations. Other probable concurrent changes are slight increases in selenium zinc and lead, and a decrease in copper content. In relatively acid conditions copper is more notably depleted from basalt. Sample 6 contains trace elements in abundances similar to those in the basalts unaffected by geothermal emanations, though mercury is commonly a little lower, ca. 0.014 ppm at other locations.

Associated with the basalts near thermal activity, which usually undergo changes as per sample 4, are pyrite, high concentrations of antimony (up to 2% Sb), mercury and erratically high copper. Anomalously high antimony only occurs near basalt and thermal waters which are warm (ca. $\geqslant 27°$).

The Taheke Basalts contain very similar mercury concentrations to the Horeke Basalt (ca. 0.015 ppm) and are less than 10,000 Y.B.P. (Mulheim, 1973). Their source may be the heat source, or part of it, for the geothermal system. The low concentration of mercury in the basalt and the small volume disallow the basalt as a significant source of mercury. The yield of mobilizable mercury is probably relatively low because much of the volatile material associated with the basalt may have escaped during eruption and cooling.

Only very weathered basalt-like material was found in the vicinity of N15/384348. This has lost a considerable proportion of all majors except iron: c.f. sample 1 of Table (A.5). The trace quantities of zinc and possibly copper have similar concentrations to local fresh basalts (which may mean that the elements have been lost in proportion to the degree of alteration). The mercury content of the rock is relatively high by a factor of 5 to 15 times that expected for a basalt in a thermally inactive area. This may be the accumulation of remnant original mercury since there are no apparent local thermal emissions. (Only 0.0008 to 0.0015 ppm total mercury was present in ground-waters emanating from basalt distal to thermal activity, and some of this mercury may come from other sources such as the natural abundance in rain, hence little mercury is leached from basalt).

d. The Lake Sediments

The sediments have the widest range of mercury concentrations of all the country rocks, including the lowest and highest concentrations. The total mercury is about 0.003 to 0.008 ppm for background levels and for anomalies it may rise to over 1% adjacent thermal activity. The corresponding cold extractable mercury (in 2 : 1 aqueous HNO_3) ranges from 0.0004 to 0.15 ppm, although it rarely exceeds 0.02 ppm (Table (A.10)). The lake sediments are a surface veneer of quartz-dominated material and hence contribute little to the thermal fluids, however due to their great permeability the sediments allow wide dispersion of mercury around the geothermal emanation, see Figures (9.1) to (9.3) which contrast with the other country rocks where mercury haloes are far more restricted.

e. Rhyolite

The Putahi rhyolite dome, which occurs 5 km west of the northern end of the basin, contains 0.01 to 0.02 ppm total mercury and falls outside the 100° C/km geotherm. Since the rhyolite is also Pliocene and cold it is unlikely to play an active part in the present geothermal system; supplying neither significant energy nor geochemical components. Several authors (e.g. in Thompson and Kermode, 1965; Ellis and Mahon, 1966) have suggested the presence of a low density acid magma or rhyolite at depth to the south-west of Ngawha Springs. There is no direct evidence for this, only the centering of a local gravity low to the south-west of Ngawha Springs.

f. Andesite

The Wairakau andesite outcrops as little as 16 km away (Kear and Hay, 1961), and is also outside the 100° C/km geotherm and contains only about 0.009 ppm total mercury. Hence the andesite is unlikely to contribute to geothermal system.

g. Summary

The Waipapa sediment group contains appreciable quantities of argillites and greywackes with significant quantities of mercury. The sediments form the basement from about 500 m depth, and by virtue of their situation and the thermal gradient form by far the major source for geothermal mercury and other geochemical components. Minor sources for geochemical components are the chaos breccia/Mata Series sediments and the Horeke Basalt which supplies iron. The chemistry of the hydrothermal system does not indicate what the heat source is, rather the chemistry reflects the presence of heated marine sediments (Ellis and Mahon, 1966) and probably some other organic material.

(9.8) ENERGY

Within about the last one million years two possible energy sources have appeared. They are the basalts and the Putahi Rhyolite; hence the possible magmatic activity present is represented by two extremes. Basalts have flowed intermittently during the last 2.3 million years (to less than 5,000 years ago a few kilometres away), however not until ca. 7,000 Y.B.P. has the basin and its environs experienced any general hydrothermal activity. Another consideration is that a virtually static energy source (magma) relatively rapidly depletes the local rocks of all volatiles (including mercury), after which no further source material is available. Hence there would be a relatively early decrease in the rate of evolution of geochemical components. However a slowly rising magma continuously penetrates fresh material, and can move up into shallow crustal levels where the rocks may not have experienced previous heating and therefore can have relatively high volatile contents. A shallow magma chamber should also cause steep thermal gradients and broad-scale heating because of the long time taken for the rise of the bulk magma (unlike for a basalt magma). Hence relatively large-scale hydrothermal cycling and geochemical movement is more likely to ensue in the presence of a slowly rising magma.

Therefore in spite of the conjectural nature of an acid magma at Ngawha it is more appropriate for a continuous discharge of energy and geochemical components than are the intermittent effusive basalt flows from a relatively static deep magma.

CHAPTER TEN THE FLUX OF MERCURY

It is clear that 'ore-grade' mercury is being deposited at Ngawha Springs, hence it is of interest to find out how much and how rapidly mercury is deposited in economic concentrations, as well as how much mercury has evolved from the associated geothermal system. Sufficient data are available to calculate the various flux components with the use of reasonable assumptions *.

(10.1) THE FLUX COMPONENTS

The mercury moved by the thermal system consists of:-

a. the total anomalous mercury present in the ground plus
b. the total anomalous mercury lost to the overlying environment, which should approximate:
c. the total mercury transported from the deep hydrothermal reservoir.

a consists of the anomalously high mercury in:-

i the cinnabar depositing region (prior to mining),
ii the country rocks,
iii the soils plus
iv the biota

b consists of the anomalously high mercury lost by:-

i the evolved gases,
ii the various waters plus
iii diffusion from the ground.

(10.2) *ASSUMPTIONS

In order to calculate the flux components several assumptions are necessary:-

i the commencement of all geothermal activity and mercury deposition was 6850 years before 1976,

ii all the geothermal fluids originate from the one reservoir,

iii similar quantities of fluids and mercury have been exhaled continuously during the 6850 years

iv all significant geothermal exhalations have been accounted.

v the geothermal reservoir starts at ca. 215° C.

a

(10.3) DEPOSITION ZONE ANOMALY

The total anomalous mass of mercury has been calculated in section (9.6) and is 620 tonne.

(10.4) THE COUNTRY ROCK ANOMALY

As discussed in section (9.5) there are three groups of correlations for depth verses mercury concentration which are characterised by the lateral distance from thermally active ground. The trends are thus grouped:-

i Distal,
ii Proximal and
iii Deposition Zones.

a. The Distal Country Rock

Using the data in Tables (A.1), (A.9) and (A.10) the quantity of anomalous mercury contained in country rock is calculated as shown in Table (9.1). The average anomalous concentration in the distal volume of country rock is 0.031 ppm of mercury (Figure (9.1)) and which yields a total mercury anomaly of almost 140 tonne.

b. The Proximal Country Rock

The proximal zone extends for several tens of metres around geothermal activity, and it contains substantially higher mercury concentrations than the distal zone. It averages 0.17 ppm and the total volume contains 240 tonnes of mercury: with the addition the deposition zone country rock, it holds nearly 260 tonne of mercury. The proximal zone holds almost twice the quantity of mercury as the distal zone, but occupies only one third of the volume (Table and Figure (9.1)).

c. The Deposition Zone Country Rock

There is little difference in concentrations of the proximal and deposition zone country rocks so the very high mercury anomalies have been included in the

TABLE (10.1) The Combined Mercury Anomalies.

Anomaly	Mass (tonnes)
Soils	4.3
Unaltered country rock	394.8
Vents to fumaroles	410
Geothermal sediments + ore shoots	70
Sub-ore-grade	64.3
Mined Mercury	85
Basal	150
Hence the total anomalous mercury at Ngawha =	1178.4 tonnes

TABLE (10.2) The Diffused Mercury

Surface Area	Diffusion Gradient	Flux of Mercury		Total
$m^2 \times 10^{-5}$	$kg\ m^{-4}$	$kg\ sec^{-1}$	$kg\ yr^{-1}$	tonnes
5.2	1.3	3.47×10^{-6}	110	750
13.9	0.44	3.15×10^{-6}	100	660
22.1	0.06	0.68×10^{-6}	21.7	150
Hence the total diffused mercury possible in 6850 years is				1570 tonnes.

above section (10.4b). The resultant total anomaly has been calculated in Table (9.1) as part of the proximal mercury anomaly. Alone, the deposition zone contains about 17 tonnes of mercury.

d. The Soil Anomaly

The mercury held in both the proximal and distal soils is also calculated in Table (9.1). Although high concentrations occur in proximal soils, the total soil anomaly is small because of the relatively small volume compared to the underlying country rock. The proximal soils contain about 1.5% of the combined proximal zone anomaly, whereas the distal soils contain ca. 0.4% of the total distal anomaly. The results respectively reflect the presence and the absence of a maximum mercury concentration near the base of the soils as indicated in Figures (9.10) and (9.11).

e. The Biota Anomaly

Although there are high mercury concentrations in plants bordering the deposition area (Table (A.6)), the total anomalous mercury present in biota is an insignificant part of the total mass-balance. By far most of the plants and animals contain less than 1 ppm anomalous mercury. The area is not heavily wooded, an average square kilometre contains between five and 100 tonnes of living material (not part of the soil); i.e. 5 to 100 g of mercury.

b

(10.5) MERCURY IN EVOLVED FLUIDS

a. Mercury Lost in Gases

Summing the product of gas flow and mercury concentration for each fumarole yields an average annual mercury flux of 26 tonne in 6.75×10^8 litres of gas (Figure (A.7) and Tables (A.12) and (A.16)).

b. Mercury Lost By Waters

Section (6.3) shows that about 17 kg (0.017 tonne) of mercury are carried from the basin each year in the streams. (The estimate neglects the decrease caused by water evaporation, and the increase caused by the increased proportion of particulate matter transported during floods).

(10.6) MERCURY LOST BY DIFFUSION

The permeation of mercury into country rock far from hydrothermal fluids

implies significant diffusion takes place, e.g. the 140 tonne of anomalous mercury in the distal zone. Near warm to hot thermal emanations many soil-gases are saturated with elemental mercury and yet continuously lose it to the air. Therefore mercury diffuses from the hydrothermal fluids through the country rock and soil into the air. Figures (9.3) and Tables (A.2) and (A.3) give the distribution of elemental mercury in soils.

The average speed of a mercury vapour atom at 25°C is 638 km/hr (Moore, 1966), a high speed in spite of the large atomic mass of mercury. Hence mercury is quite mobile under the conditions prevalent in the Ngawha Basin, thus the diffusion of the element may be an important part of the total mercury flux. Kinetic theory can be used to calculate the diffusion flux of mercury. The applicability of the approach is almost ideal because mercury is relatively inert and moves as single spherical atoms. Fluxes and the intermediate calculations from kinetic theory compare well with known data for other substances, and the final flux fits the mass-balance to within 16% of the estimated total flux (see Table (10.3)).

The method used to calculate the flux is set out below and follows the general principles of kinetic theory (e.g. Chapter 7 in Moore, 1966).

Definition of Variables and Symbols

Symbol	Function	Dimension
J	Total mass diffused	kg
j	Diffusion flux	kg m^{-2} sec^{-1}
D	Diffusion constant	m^2 sec^{-1}
z	Vertical distance	m
$\frac{d(\ )}{dz}$	Concentration gradient	kg m^{-4}
$\bar{c}$	Average speed	m sec^{-1}
λ	Mean free path	m
x	Mole fraction	-
N	Number of particles per unit volume	m^{-3}
d	Particle diameter	m
T	Temperature	K
M	Molecular weight	a.m.u.

$$J = \left(\sum_{i=1}^{n} j_i \times \text{area}\right) \times \text{time} \qquad (10.1)$$

$$j_i = D \frac{d(Hg^o_i)}{dz} \qquad (10.2)$$

$$D = \frac{1}{3} \lambda_{gas} \bar{c}_{gas} x_{Hg^o} + \frac{1}{3} 2_{Hg^o} x_{gas} \qquad (10.3)$$

$$\lambda = (2^{\frac{1}{2}} N d^2)^{-1} \qquad (10.4)$$

$$\bar{c} = \frac{8 R T}{M} \qquad (10.5)$$

Since the mercury concentration in the soil-gas is less than 13 μg/l (1.3×10^{-11} kg m^{-3}):

$$x_{Hg^o} \ll x_{gas} \qquad (10.6)$$

and

$$x_{Hg^o} + x_{gas} = 1 \qquad (10.7)$$

Therefore $x_{gas} = 1$ (10.8)

Thus equation (10.3) becomes:

$$D = \frac{1}{3} \lambda_{Hg^o} \bar{c}_{Hg^o} \text{ , the diffusion constant} \qquad (10.9)$$

for mercury at low concentrations in a gas. Hence the diffusion constant depends only on the average speed of a mercury atom and its mean free path in the gas.

From equation (10.5) the average speed of a mercury atom at the ambient surface temperature of 15° C for the Ngawha Basin is:-

$$\bar{c} = \frac{8 \times 8.314 \times 10^3 \times 288}{200.59} \quad \text{m sec}^{-1} \qquad (10.10)$$

$$= 174 \quad \text{m sec}^{-1}$$

The mean free path (λ) of mercury depends on the number of gas molecules per unit volume (N) and the average molecular diameter of a mercury atom plus a gas molecule ($d = \frac{d_{Hg^o} + d_{gas}}{2}$). Substituting values for these from Weast (1975, F 199 - 206) equation (10.4) becomes:-

$$\lambda = (2 \times \times 2.54 \times 10^{25} \times 3.2^2 \times 10^{-20})^{-1} \quad m \qquad (10.11)$$
$$= 8.9 \times 10^{-8} \quad m$$

Therefore

$$D = \frac{1}{3} \times 8.9 \times 10^{-8} \times 174 \quad m^2 \text{ sec} \qquad (10.12)$$

$$= 5.17 \times 10^{-6} \quad m^2 \text{ sec at } 15°C.$$

The major problem now is choosing the appropriate concentration gradient of mercury between soil and air. The very high gradient at the interface does not reflect the rate of mercury escape in most cases. The gradient in the soil is commonly greater than that in the country rock below, which supplies most of the mercury. Since the escaping mercury cannot exceed the supply (or else the soils would be depleted in mercury), one can reasonably assume that a steady state equilibrium exists between the supply and the escape; i.e. the supply is the rate determining step for the escape. The porosity of the lake sediments (which cover most of the basin) is high, and the contained gas has similar mercury concentrations to that in the lowest parts of the soils. Hence the concentration gradient used was the linear gradient from the base of the soil to near the surface (i.e. $\frac{d\ (Hg^o)}{dz}$ is constant). The soil gas is assumed to be CO_2-rich air, however this cannot cause much error.

Measurements of elemental mercury in soils are given in Tables (A.2), (A.3) and (A.10). The average gradients used are quoted in Table (10.2) where the diffusion fluxes are also calculated. The total flux is 0.24 tonne per annum, which amounts to 1590 tonne of mercury lost into the air during 6850 years.

a. Basal Diffusion Anomaly

Below the Ngawha Basin are convecting fluids which are the origin of the springs (Giggenbach and Lyon, 1978). In consequence the deep fluids which have a high mercury content are able to diffuse mercury from themselves into the surroundings. As the fluids circulate some fluid escapes via springs and some by diffusion, the rest remain part of the convection cell and redescend. It is only those fluids which escape that can contribute to ore deposition (and can be determined by surface-flow measurements). Therefore the mass-balance of the deposition processe(s) depends only on mercury in the escaping fluids and includes all mercury attributable to the escaping (spring) fluids.

TABLE (10.3) Total Mercury Flux in the Ngawha Geothermal System.

Duration of thermal emissions to 1976		6850 years	
INPUT			
Gas flows currently (1300 l min^{-1})		6.84×10^{8}	l yr^{-1}
Total gas evolution		4.68×10^{12}	l
Mercury concentration in deep gas		7.70×10^{2}	$\mu g\ l^{-1}$
Total mercury evolved	*	3.59×10^{3}	tonne
Geothermal water flow		1.89×10^{7}	l yr^{-1}
Total water evolved		9.73×10^{10}	l
Maximum mercury in water (calculated from v.pr.)		0.20	ppm
Total mercury delivered by water	*	26	tonne
Annual total mercury influx		0.53	tonne yr^{-1}
Total mercury in combined fluids	*	3.62×10^{3}	tonne
OUTPUT			
Fumarolic mercury loss to air		26	tonne yr^{-1}
Total fumarolic mercury loss	*	1.8×10^{2}	tonne
Fluvial mercury loss from basin		17	kg yr^{-1}
Total mercury lost by streams	*	1.15×10^{2}	tonne
Diffusion of mercury into air		0.235	tonne yr^{-1}
Total mercury lost by diffusion	*	1.6×10^{3}	tonne
Combined mercury anomalies	*	1.18×10^{3}	tonne

Hence the total accounted output of mercury is ca. 3060 tonnes,
and the mercury deficit (input-output) is ca. 560 tonnes or
about 15½% of the input.

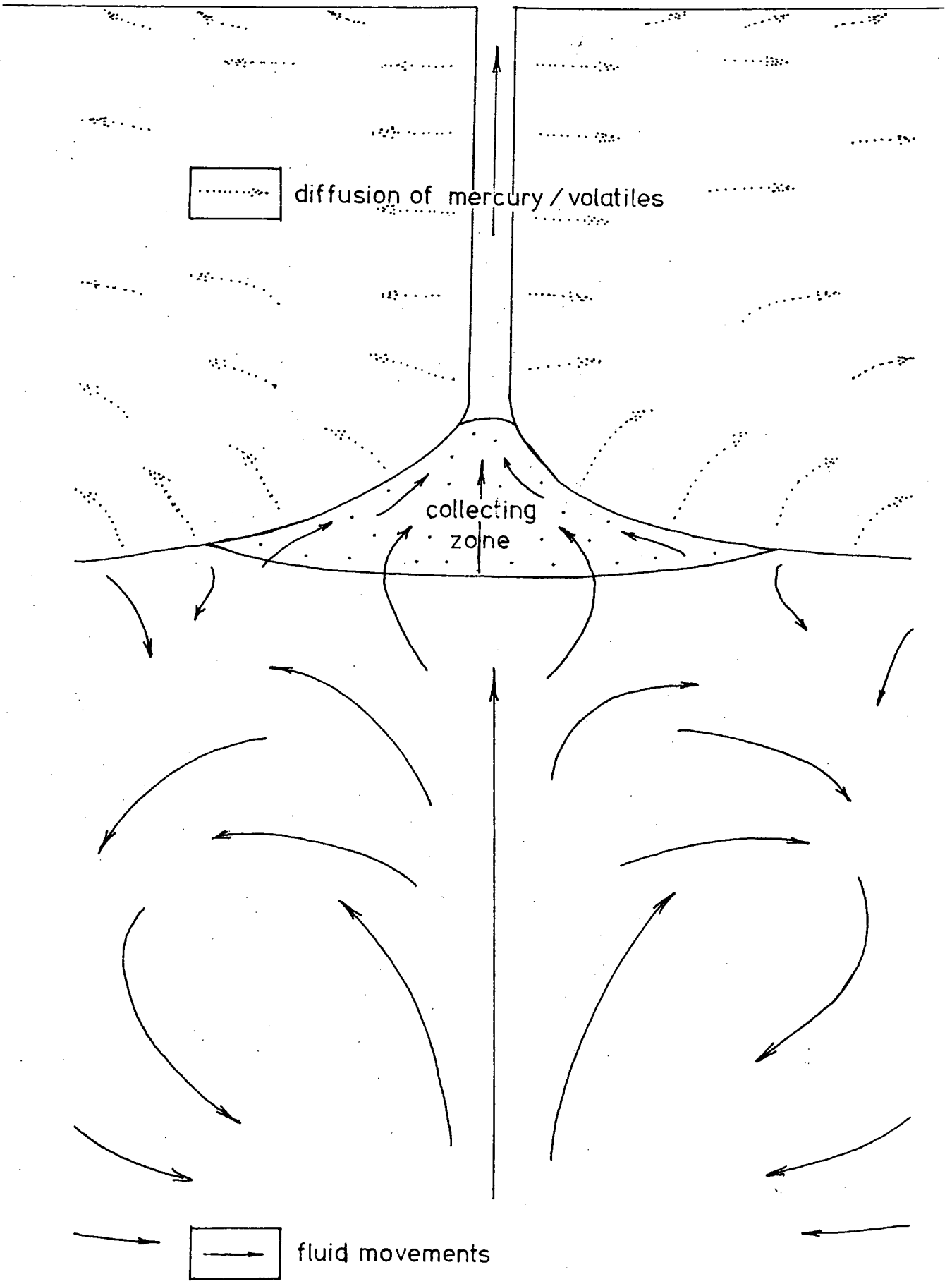


Figure (10.1) The Hydrothermal Convection System

In particular the rising fluids contribute to the large halo of anomalous mercury surrounding them, however some of the halo may also result from the diffusion of mercury from the upper boundary of the deep hydrothermal cell. Consequently one neglected area of mercury loss is that from the perimeter of the convection cell, where mercury diffuses into ground adjacent to the cell. The mercury so lost from the deep fluids may cause decreases in the mercury found in some hot springs. The basal anomaly is essentially a continuation of the proximal zone anomaly. The pertinent source fluids for both anomalies are those which are on a direct path to the surface via the springs: the basal anomaly is caused by the fluids which no longer circulate and are not yet rising in the 'hot spring plumbing'. The similarly caused proximal anomaly was calculated for the same fluids as they rise. Any fluids not directly moving towards an escape route are not part of the relevant ore-fluids and must be omitted from the mass-balance.

The upper part of the convection cell where escaping fluids leave the circulation system and move toward the fissures is depicted in Figure (10.1) and is called the 'collection zone'. Thus the proximal anomaly (about the rising fluids) continues across the collection zone and into the diffusion anomaly due to the mercury-rich fluids around the rest of the hydrothermal convection plume. At the surface the minimum extent of the collection zone is marked by the areas containing centres of mercury emissions (assuming vertical fissures), which occupy an area of slightly more than five square kilometres. Pro rata extension of the anomaly where it lies at the base of the distal zone yields an extra 150 tonnes of mercury. (Any other anomaly below the basin can be attributed to mercury from fluids still convecting). A more refined estimate of the anomaly with present data is impossible.

c

(10.7) TOTAL MERCURY FROM THE RESERVOIR

Calculated from the data in Table (10.3), the total amount of mercury carried in the geothermal fluids is about 0.52 tonnes in gases and about 0.0038 tonnes in the coexisting liquid phases each year; i.e. a total of ca. 3620 tonnes has been carried from the 'mercury reservoir' by deep geothermal fluids into the Ngawha Basin environment, and 99.3% of all the mercury has been transported in the gas phase of the thermal fluid.

TABLE (10.4) The Relative Mercury Flux

	tonnes	percentage of input	percentage of output
INPUT			
Gaseous	3590	99.3	117
Aqueous	26	0.7	0.85
OUTPUT			
Fumaroles	180	5.0	5.9
Aqueous	115	3.2	3.8
Diffusion	1590	44.0	52.0
Deposition Zone	620	17.1	20.3
Country Rock	400	11.1	13.1
Basal	150	4.1	4.9
Biota	0.1	0.0028	0.0033
DEFICIT (input-output)	560	15.5	18.3
ORE	160	4.4	5.25

(10.8) DISCUSSION OF THE FLUX MODEL AND CALCULATIONS

The independently estimated total mass of mercury carried by the deep ore-fluids (input) and deposited by or lost from the fluids (output) are ca. 3620 and 3050 tonnes respectively (Table (10.3)). The difference is 560 tonnes or 15½% of the input which is within the probable bounds of the accuracy for the flux model. The 15½% difference means that the estimated sum of the mercury anomalies in gases, waters and rocks fall short of the estimated total (maximum) amount of mercury transported by the total geothermal fluid. Certainly then, at least 60% of all the mercury originally carried in the ore-fluids has already been lost to the environment outside the Ngawha Basin.

The surface diffusion loss is 44% of the total input and 52% of the total output Table (10.4), therefore it is the largest factor in the movement of mercury from the deposition zone to the rest of the environment. It is also the least reliable calculation due to the difficulty of obtaining concentration gradients which are known to be appropriate, subsequently the error is difficult to quantify. However the diffusion loss appears to be within 35% of the probable range because the 560 tonnes difference between the total fluxes is 35% of the estimated diffusion flux and the basal anomaly is a minimal estimate in the total flux. The literature available does not yield any data useful for comparison.

The diffusion calculations are probably conservative because the immediate surrounds of several fumarolic centres are saturated with mercury and have not been included as such. For most of the proximal zone soils, after the soil-gas has been blown off, the new gas gains considerable mercury from the soil within a few minutes and commonly contains more than 50% of the concentration present in the previous equilibriated gas. At the air-soil interface the air to soil-gas mercury concentration gradient is usually much larger than that below, because of the small distance between the air and soil-gas (which has a substantially higher mercury concentration). Thus the relative ease of replacement of lost mercury and the steep surface concentration gradients imply higher rates of mercury diffusion than those calculated.

An alternative estimate of the diffusion flux was made using the average concentration gradient from water a few metres above the ground and equilibriated with air (during non-windy periods) and the surface soil-gas below. The flux was ca. 350 kg/year and 2,400 tonne for 6,850 years. However the accuracy and the applicability of the approach are less sound than the previous method of calculation. For in

practice it turned out that the concentration gradient depended on only the inverse of the height of the water above the ground and the soil-gas concentration: this means that the gradient depends on the sample height. The only exceptions were in very sheltered depressions where the water was close to the ground . The presence of the mercury in the equilibriated water at least shows that mercury does diffuse from the ground into the air.

Perhaps the strongest argument for substantial diffusion of the order calculated is that without it there must be a huge positive anomaly of (elemental) mercury confined to the fumarolic areas. The quantity of mercury would be close to the difference between the input and the fluid losses, some 2,700 tonnes more mercury than currently present within a short distance of the fumaroles. The economic mercury would be more than an order of magnitude higher than it was in 1895!

The lateral migration of mercury through the porous lake sediments is probably the major supply of mercury for atmospheric diffusion within the basin. Outside the proximal zone the radial concentration gradients are very low (ca. 0.002 μg/l/m on average). This infers that some mercury diffuses from the underlying chaos breccia and is only a significant contribution where mercury concentrations are very low.

The anomalous mercury represents about 33% of the total mercury input, and 40% of the total output (Table (10.4)). The 560 tonne mercury deficit is 48% of the 1170 tonne anomaly. Thus the total anomalous mercury is a major part of the total mercury flux and an accurate estimate is important. Fortunately the major portion (72%) of the mercury anomaly lies in the best studied zones, around the thermal areas. The mercury content at depths beyond halfway to the convective portion of the hydrothermal system can only be estimated on the basis of trends in the area and the properties of mercury, but there is no reason to expect or suspect anomalously high concentrations of mercury outside the feeders to the fumaroles (vent zones). Other mercury deposits also have a rapid fall-off in anomalous concentrations away from the deposits and the ore-solution conduits (e.g. Bradshaw and Koksoy, 1968; Hoggins, 1972).

About 830 tonnes of mercury are held in the thermal areas and 80 tonnes in the upper part of the country rock plus soils, making about 900 of the 1170 tonnes of the anomalous mercury: this leaves 300 tonnes to any conjecture. The 300 tonnes of mercury is likely to be too small rather than too big, and any large increase in the anomaly is unlikely to come from the ore-fluids, but from the diffusion of mercury from the convection cell (Figure (10.1)).

Although it is probable that the total mercury anomaly is larger, the very low anomalous mercury concentrations beyond the distal zone and the rapid general exponential fall-off in mercury concentrations with distance from thermal emanations ensures that the anomalous mercury halo significantly decreases with distance from the thermal activity. For instance the closest ten square kilometres outside the distal zone probably contain less than 25 tonne of anomalous mercury.

150 tonne of anomalous mercury was estimated to be present below the proximal zone and caused by the diffusion of mercury from fluids about to enter the fumarole 'plumbing'. The estimate was based on diffusion in the proximal zone at near surface temperatures. Since the temperature of the convection cell boundary is ca. 215°C, the diffusion constant(s) for mercury are 30% greater than at 25°C. Hence more mercury may diffuse further than estimated, but no more than about 60% extra mercury.

The depth to convection below the valley is assumed to be the same as indicated by the temperatures calculated from D/H isotope fractionation (Giggenbach and Lyons, 1977). The approach assumes a relatively sharp boundary around the upper portion of the convection cell and that the waters rise fast enough to prevent significant isotope re-equilibriation. Hence the effective cell edge could be deeper. The upper D/H temperatures are near 250°C, which is equivalent to a total anomaly of ca. 1450 tonnes (cf. 1170). The diffuseness of the convection boundary is not calculable, however even where only minor convective flow occurs, the extra anomaly is likely to be transient convected mercury only partially able to diffuse away (and yield a small fraction escaping via the fumarole plumbing). Hence the estimated total mercury anomaly is probably a reasonable minimum.

The fumarolic loss is probably accurate to within 20%, and is the most accurately determined because all the major contributions were directly measured.

The input estimate which is based on the highest mercury concentrations in bore-waters (0.21 ppm) and gases (770 μg/l) from the Tuwhakino area are probably not grossly wrong unless there have been considerable changes in gas flow and temperatures. Diffusion of mercury from deep fluids during their migration upwards indicates that gas leaving the hydrothermal reservoir contains more mercury than measured at the surface. However the percentage of mercury lost from the most vigorous hot emissions is assumed to be negligible due to the relatively fast rate of ascent of fluids in the Tiger-Tuwhakino area and the very steep thermal gradients (ca. 600°C/km).

Only deep drill-hole analyses can test the assumption quantitatively.

The 16% deficit in the mercury output is equivalent to a change from 770 to 650 μg Hg°/l gas coming from the reservoir. The concentrations correspond to respective mercury saturation temperatures of ca. 76 and 73°C; yet temperature fluctuations up to five degrees may occur in fluids less than 30 metres deep. However where hot ground is constantly saturated with mercury and/or accumulating the liquid, the temperature must be at or below the dew-point of mercury, hence it is unlikely that the maximum concentrations found in the fluids are more than ten percent in error of the concentrations of the samples sought. Where temperatures are constantly above 76°C, fluid saturation to 75-76°C strongly supports the presence of similar mercury concentrations in the deep fluid, particularly where similar temperatures have reigned for more than 80 years.

To produce the estimated total of 3,620 tonne of mercury produced from the source materials below Ngawha, 10 - 35 km^3 are needed from an estimated source volume of over 130 km^3 within the 215° isotherm (calculated from Giggenbach and Lyon, 1977 and Banwell, 1965). The source volume excludes the magma and the chaos breccia. Hence there was at least four times more mercury present in the source than has been evolved todate, and over five times if the chaos breccia contribution is included as part of the source. Thus about 20,000 tonnes of mercury was originally available for transport into the deposition zone(s) of the Ngawha geothermal system. Therefore by extrapolation of the current average deposition efficiency, the economic concentrations of mercury will eventually total almost 1,000 tonnes when all the mercury has been evolved from the source.

Of the five assumptions required (Section 10.2)), the only assumption difficult to justify, and which is probably wrong, is that there has been a constant mercury flux throughout the last 6,850 years. During the first few years of thermal activity there was probably significantly greater emission rates than at present, hence early mercury evolution was probably higher. Since mercury is very mobile the majority of the interval may have had a steady state operating which would dominate overall. (The high mobility should cause a fast tendency to a steady state, or a state of slowly decreasing mercury concentration after an early high maximum). At present it is impossible to make any estimate of flux changes with time. If there has been a large decrease in mercury flux over a substantial proportion of the time interval, then the assumption would lead to an underestimate in both the input and the output ($\bar{c}$ will which at least partially cancel) and to an overestimate of the deposition efficiency.

The above discussions show that the mass-balance is compatable with the available data and that the fluxes are realistic. Hence the modelling of the thermal system is reasonable and the 560 tonne deficit would seem mostly attributable to the conservative diffusion model estimate.

(10.9) POST MERCURY-EVOLUTION

Once mercury has ceased accompanying the thermal fluids there will be no supply of mercury to the transient portion of the mercury anomaly which will continue to diffuse until none of the mobile mercury is left. Hence the anomaly will decrease. Similarly mercury in the deposition zone will decrease near fumaroles should gases continue to evolve because cinnabar has co-existing mercury vapour (Krauskopf, 1951; Weast, 1975) which passing gas can take away. However the low vapour pressure of cinnabar will cause the attrition of the cinnabar deposits (due to the dissociation process)to be much slower than the deposition of cinnabar.

Further losses of cinnabar are due to photolysis and erosion. At Ngawha, Steamboat Springs (USA) and the Puhipuhi deposits (New Zealand) it was noticed that cinnabar exposed to sunlight gradually decomposed; the mercury evaporates and the sulphur oxidizes. (The Puhipuhi and Steamboat Springs cinnabar 'sinters' may also change from bright red to grey due to trapped elemental mercury). Erosion is most active in the creek beds and environs at Ngawha where most of the richest ore is deposited and is thus probably the greatest attrition factor operating on the Ngawha mercury deposits.

Currently reducing conditions caused by the geothermal emanations minimize the oxidation of cinnabar, and soluble mercury can be trapped as cinnabar by bacterial action. Once geothermal activity wanes sufficiently, surface waters will cause much more oxidative attrition of cinnabar, though probably only at very shallow depths because of the independent presence of reducing organic materials, Fe^{2+} and the limited access of oxygen. Oxidation of cinnabar by Fe^{3+} (Burkstaller, McCarty and Parks, 1975) would mainly occur at the surface and is hindered until H_2S evolution ceases.

(10.10) SUMMARY

Of all the mercury entering the deposition zone of the thermal system more than 60% of it is completely lost to the atmosphere and streams via diffusion, exhalation, and dissolution. 38% of the mercury (output) is in the ground and forms the

anomaly, but because of diffusion a significant proportion of the anomaly is transient (as Hg^o). Analyses also indicate that at least 20% of the total anomalous mercury is present as Hg^o: the percentage is probably higher since most adsorbed mercury is probably elemental mercury (e.g. in soils). The major portion of the mercury anomaly is in the dispersion halo, which is attributable to diffusion, the greatest single flux factor. Only 5¼% of the total mercury or 14% of the mercury anomaly has been deposited in economic concentrations, i.e. the deposition of cinnabar at Ngawha Springs is inefficient, and in ca. 27,000 - 30,000 years all the mercury will have been extracted from the current source to yield 800 - 1000 tonne of economically recoverable mercury as cinnabar in ore averaging ca. 0.25% mercury.

Too much mercury has been deposited as cinnabar (160 t) or exhaled by fumaroles (180 t) to be accounted for in terms of any known combination of possible aqueous species, since the total aqueous mercury flux is no more than 26 tonnes. This fact strongly supports the argument that the bulk of the mercury is transported by the gas phase of the geothermal fluids of Ngawha Springs.

CHAPTER ELEVEN CONCLUSIONS AND SUMMARY

(11.1) A PRECISE OF MERCURY DEPOSITION AT NGAWHA

At Ngawha Springs, New Zealand mercury is currently depositing as cinnabar from the element transported in gas-dominated 'ore-fluids'. The fluids are mercury saturated up to ca. 76°C and carry 99.3% of all the mercury in the gas phase. Mercury species other than the element are negligible, they represent less than 0.15% of the mercury in the aqueous phase and less than 0.1% of the mercury in the vapour phase. The deposition of the cinnabar has been observed to form by a mechanism involving:-

(a) The oxidation of Hg^{o} to Hg^{2+} in either

- i aqueous acid-oxidizing media,
- ii neutral-oxidizing dilute brines or
- iii weakly acid - weakly oxidizing dilute brines with

(b) Sulphide species produced by

- i dissolved geothermal hydrogen sulphide or
- ii bacteriogenic sulphate reduction

Marcasite and pyrite are also depositing, both form from the reaction of iron leached from local superficial basalts and sulphide species produced by (b) above. Commonly marcasite (with traces of other metal sulphides) pseudomorphs vegetation debris, and after oxidative destruction yields residual cinnabar-rich lenses. The marcasite and cinnabar deposition dominantly occur in open systems of mixing fluids where oxidation is caused by the reaction:-

$$4H^{+} + O_2(g) + 4e^{-} \rightleftharpoons 2H_2O \qquad E^{o} = 1.23\,v.$$

The geothermal mercury is produced by the pyrolysis of local basement marine sediments. The mercury ascends into the Ngawha Basin along three possibly active north-east striking faults which have had associated geothermal emanations during the last 6850 years and currently lie within an area having a geothermal gradient of 350° - 625°C/km to depths of ca. 500 m. The quantity of mercury evolved from the deep geothermal cell into the basin and environs averages about 0.53 tonnes per annum with an associated fluid flow of 7×10^{8} l gas and 2×10^{7} l solution each year.

About 5¼% of the mercury evolved forms ore whilst ten times as much (52%) diffuses through the country rock into the atmosphere. The total mercury anomaly (including the large low concentration dispersion halo) holds about 38% of all the mercury, the remaining ca. 10% is lost by emanating fluids.

All the cinnabar lies within ca. 25 m of the surface and the economic cinnabar restricted to depths of less than ca. 5 m. Generally maximum mercury concentrations in areas of high anomalies ($\geqslant$ 50 ppm Hg) are located near the top of the water-table. By comparison with the similar Sulphur Banks (USA) deposits, which are estimated to be ca. 100,000 years old (White and Roberson, 1962), the present rate of mercury deposition at Ngawha Springs would yield a very similarly sized deposit in the same time. However, judging from the volume of source material in the current geothermal regime below Ngawha, there will be no more than about 1000 tonnes of ore produced.

Soils throughout much of the Ngawha Basin contain anomalous mercury concentrations, especially in the top-soil and horizons containing montmorillonite. By contrast kaolinite-rich horizons have little anomalous mercury and very low concentrations of mercury. Of all the mercury species studied, the organomercurial concentration shows the most regular correlation with depth: it rapidly decreases. Anomalous elemental mercury displays the least dependence on rock-type and is strongly dominated by the proximity to geothermal activity, thus suggesting the origin for the mercury. Near thermal activity the element commonly shows a small increase with depth unless the area is underlain by a basalt flow, the flows are apparently relatively impermeable to mercury.

The 'hydrothermal' iron minerals occur only close to basalt; marcasite dominates shallow depths (ca. $\leqslant$ 5 m) and pyrite dominates below. The marcasite forms as a black and commonly colloidal FeS precipitate which diagenetically changes to FeS_2 in situ which may encase the sulphurous gases from which forms. The encasing tubes grow mostly via their outer surface.

In summary the mass-balance model developed for the deposition of cinnabar at Ngawha Springs is:-

1. A shallow magma is present below the Ngawha Basin and environs
2. The magma causes regional high temperatures in the country rock and some pyrolysis.
3. Mercury is dominantly evolved as Hg^{o} from the country rock by pyrolisis.

4. The mercury accumulates in a convection cell ($\geq 215^{\circ}C$).
5. The entire geothermal component emanating at all springs is from the cell.
6. The geothermal fluids rising from the cell are gas-rich.
7. The gas phase of the rising fluid transports most of the 'ore-solution'
8. Elemental mercury diffuses from the cycling and ascending fluids
9. The thermal gradients between the surface and the cell are linear
10. The dew-point of mercury vapour is reached in all springs
11. All significant deposition of cinnabar occurs within 30 m of the ground surface.
12. Cinnabar deposition is controlled by oxidation processes.
13. The diffusion of mercury is least inhibited by the superficial lake sediments.

(11.2) MERCURY DEPOSIT CHARACTERISTICS AND THE MODEL

The model developed for mercury deposition at Ngawha Springs inherently explains the characteristics common to mercury deposits world-wide. Another consequence of the model and its plausibility at most other deposits are optima for the deposition of mercury; i.e. conditions which are most favourable (or necessary) to yield an economic deposit.

The characteristics of mercury deposits (listed in chapter two) are mostly concomitant with the thesis developed and are briefly explained in terms of the thesis models below:

1. Deposits are commonly associated with hot springs or fluid inclusions.

The presence of water (liquid) is needed as a medium in which the oxidation mechanism may proceed and in many cases to transport the mercury. Water (like mercury) at moderate to high temperatures has a substantial vapour pressure, therefore it is volatile and likely to accompany elemental mercury due to the overlap in physical behaviour. (The volatility of water depends on the solute content, hence strong brines are not expected to accompany mercury unless it is somehow held (probably by complexation) in solution).

2. Deposits mostly form near tectonically active zones. In such areas there is a much greater probability of a suitable thermal anomaly existing.

3. Few deposits are pre-Cretaceous (and generally there are more deposits with decreasing age).

Cinnabar has a small mercury vapour pressure and therefore dissociates progressively as the mercury diffuses away causing cinnabar deposits to dissipate. The dissipation is more rapid with increasing temperature. (Capping a deposit or surrounding it with a mercury-impermeable rock reduces or stops the dissipation. Notably Almaden, the largest and one of the oldest mercury deposits is virtually basalt-bound. At Ngawha intact basalt flows are also relatively mercury impermeable).

4. Deposition occurs in areas of high surface temperatures and anomalously high geothermal gradients.

5. Most mercury deposits occur at shallow depths.

Shallow deposits are strongly favoured by the necessity to have accessable oxygen. High temperatures prohibit mercury deposition, hence in areas of high thermal gradients only shallow deposition sites are feasible.

High geothermal gradients are required so that mercury can be mobilized at depths where the country rock is unlikely to have had previous high temperatures which readily deplete the mobile mercury. Relatively high surface temperatures are probably only a side-function of the high geothermal gradient and emanating deep fluids. It is doubtful that high surface temperatures are needed.

6. Many deposition fluids are CO_2-rich.

Carbondioxide is a volatile (like mercury and water) and is therefore likely to accompany mercury where both are produced from the same source. CO_2 may also be an advantageous carrier gas for mercury is far more soluble in gas phases than liquid phases. The gas should also help remove mercury produced by pyrolysis in a manner similar to steam distillation. Nevertheless CO_2 is not essential as long as some other volatile(s) is(are) present.

7. The mercury and sulphide concentrations of springs do not correlate.

Elemental mercury does not directly complex with sulphur species and its solubility is independent of sulphur species concentrations, hence no correlation is expected.

8. Relatively high concentrations of ammonia and boron (HBO_2) occur in many springs.

The high concentrations appear to merely reflect the presence of marine sediments undergoing pyrolysis. The fact that the two compounds are fairly volatile causes them to be associated with mercury.

9. Waters have mercury concentration between 0.0001 and 2.3 ppm. If mercury accompanies any fluid(s), then it should be present in all phases according to the partition coefficients. (The relative quantities of the fluid phases and temperature will determine which is the major transport phase. However some mercury must be present in the water to allow the deposition mechanisms to proceed, and it is doubtful that efficient kinetics and/or transport can occur if the mercury concentration is below ca. 0.001 ppm. At and below the concentration probably only minor mercury deposits can form).

10. Mercury is common in the hot spring gases.

Any gases present should contain appreciable mercury or else transport is inefficient. (In recently non-depositing springs mercury in the gases may largely come from cinnabar dissociation, however for temperatures below 150°C the vapour pressure of mercury over cinnabar is much less than the levels of mercury measured or indicated by the literature).

11. pH is commonly between 6 and 8.5.

Since the oxidation reaction requires the presence of H^+, it is most unlikely that deposition can occur in alkaline solutions.

12. Organic materials are a common association.

Sediments commonly contain at least traces of biogenic materials which under pyrolysis yield volatile hydrocarbons which may accompany mercury. A second, probably less common organic association is due to cinnabar formed via the pseudomorphing of organic materials, where not all the available organic material is consumed by the bacteria.

13. Deposition temperatures lie between 25 and 200°C. Near and above 200° cinnabar has an appreciable mercury vapour pressure which is more likely to

cause it to slowly enter the geothermal fluids than be deposited from them. Cinnabar formed via pseudomorphing reactions occurs at temperatures as low as 24 °C: it is probable that in order to get enough mercury to notice it deposit as cinnabar, that sufficient (hot) spring water must mix with cooler aerated water (to oxidize the mercury). that cooler temperatures have not been found. (At temperatures below ca. 30° transport of mercury is severely limited, even in gas-rich geothermal fluids).

14. Pressures are commonly below 30 atmospheres.

Since oxygen is required for the cinnabar deposition shallow depths ~~and~~ hence low pressures are most favoured (30 atm $\simeq$ 300 m hydrostatic load). Another important factor is that steep thermal gradients, and especially in areas of high surface temperatures, also prohibit large depths of deposition in order that temperatures do not exceed 200° C.

15. Broad dispersion haloes of mercury are common.

Since elemental mercury is present and very mobile it diffuses readily through permeable ground. Probably for all deposits a major loss of mercury from the deposition zone(s) is caused by diffusion which yields the large haloes. In moribund deposits haloes are maintained to some extent by the diffusion of mercury from cinnabar dissociation.

16. Cinnabar is the major mercury mineral.

Cinnabar is one of the most insoluble and kinetically and thermodynamically stable compounds known at low temperatures, consequently even the presence of trace quantities of sulphide species which can cause cinnabar to form will do so at the expense of probably any other mercury compound.

17. Few other sulphide minerals are associated.

The major reason is that no other chalcophile metals are so volatile under the probable range of transport and mobilization conditions. Hence mercury will separate from the other metals because it favours the more volatile phase.

18. Few deposits are large.

The hot element is so mobile that a large proportion of it diffuses away and is lost from the deposition zone (unlike other metals which are constrained to solution or

deposition). Hence the efficiency of mercury deposition is poor, so relatively small deposits should result.

19. There is a large variety of wall rocks.

The mechanisms for deposition do not involve the wall rock, nor is there any reason for them to interfere, except perhaps carbonate rocks and acid solutions. Reactions are usually 'too fast' for the rock to have effect. Generally the deposition site rock(s) simply provide a medium in which the mercury-rich and the oxygenated fluids may mix.

20. There is a high correlation with marine sediments.

Aqueous sediments provide the most viable source for easily mobilized mercury. (Other sources are not excluded, but are less favourable).

21. There are probably no submarine formed deposits.

Water inhibits the free movement of air, and since most deep bodies have slow internal currents and biotic activity which consumes oxygen, the bottom water commonly verges towards reducing. Hence there is likely to be insufficient oxygen available where such waters are in contact with otherwise suitable mercury deposition conditions.

22. The deposition fluids are commonly 'dilute brines'.

The volatility and mobility of mercury ensure that most of the mercury leaves a hydrothermal cell long before the chloride concentration is able to build up.

23. A number of important deposits are associated with deep sediment piles or/and chaotic rock assemblages.

Large piles of sediments simply provide a large source for mercury. (Notably piles of sediments are most likely to form in trench-like areas associated with tectonism which are generally the most probable regions to develop a geothermal anomaly). Chaotic rock assemblages are probably no more a suitable source (if at all) for mercury than other rocks, but rather reflect a large amount of local 'tectonic' movement in faulted areas more suitable for easy penetration by fluids.

(11.3) GENERAL REQUIREMENTS FOR DEPOSITION

From the mechanisms and processes involved with mercury deposition at Ngawha, general criteria can be derived which explain the peculiarities of global mercury deposits and indicate otpimum conditions for economic deposition.

In order to deposit mercury by the mechanisms occurring at Ngawha Springs (and other localities), there must be:-

a. An Energy Source
b. A Mercury Source
c. A Transport Medium
d. A Deposition Medium
e. Oxygen
f. Water
g. Sulphur

There are also a number of other factors which enhance deposition.

a. An Energy Source

An energy source (or magma) which merely supplies heat is indicated by the large variety of igneous rocks which are associated with mercury deposits (e.g. Moiseyev, 1971). This does not exclude the possibility of some magmatic mercury sources. The distribution of mercury deposits follows the active tectonic plate margins on land, up to ca. 300 km from the plate boundaries. (A few deposits lie in other areas of magmatic activity). All presently active deposition sites where data is available have very steep geothermal gradients (eg. White, 1967), and the freezing-point temperatures of igneous rocks lie between 600 and 1150° (Painter, 1973) (ultrabasics are rarely associable with mercury deposition). Hence the magma depths range from 3 - 10 km for most deposits when compared to known and probable average geothermal gradients of 100 - 500° C/km.

The size of the magma bodies is commonly unknown. Geophysics and/or geology studies may give some idea of the areal extent, which is probably between 3 - 8 km^2 at Ngawha. The 'thickness' and volume are unknown, however using the heat flow data of Banwell (1965), ca. 7.3 x 10^3 kcal/sec has been lost for at least 6850 years. Hence about 3.75 km^3 of magma is required to supply the heat. However, the currently high thermal gradient and temperatures imply that cooling has not pro-

ceeded by more than about 25% for an average basalt/granite magma. (Some isotopic and chemical equilibria give temperatures in the range 400 - 620° C, (Giggenbach and Lyons, 1977)). Therefore a substantially larger volume of magma is present, at least 15 km^3. 15 km^3 is a reasonable quantity of magma for an average small commercial mercury deposit; when all the Ngawha magma has cooled, the deposits could contain about four times the mercury present prior to mining, i.e. ca. 600 tonnes (17,000 flasks) of economically recoverable mercury. The volume estimate thus suggests that a 2 - 4.5 km diameter magma chamber such as below Ngawha Springs is a minimum energy spread for a commercially viable cinnabar deposit.

b. A Mercury Source

Analytical data (Fleischer, 1970; Wedepohl, 1972) imply that almost any sedimentary, igneous and low-grade metamorphic rock could be a source for mercury. By contrast the temperature range in which the mercury is liberated is considerably more restrictive of potential sources. Other important factors are the quantities of potential sources and the prevailing temperature regime: in particular the volume with sufficiently high enough temperatures to liberate the mercury. The latter is determined by the way in which the mercury is held (Fedorchuk, 1961; Ozerova, 1962 and Bradshaw and Koksoy, 1968). Adsorbed mercury can be liberated in significant concentrations by about 120°, and nearly all of it is liberated at 250° C. Therefore significant adsorbed mercury is unlikely to be present in (igneous or metamorphic) rocks which have been above 150 - 200° C for long intervals of time. Other forms of mercury in rocks require much higher temperatures for mobilization, usually above 250° C, and as high as 600° C in some common metal sulphides (Ozerova, 1962 and Fedorchuk, 1961). Since fine-grained materials can adsorb more than coarse-grained materials (w/w), then previous information suggests that fine-grained sedimentary material is the most suitable source for easily mobilized mercury. (Fine-grained sediments commonly have relatively high mercury concentrations). The release of adsorbed mercury at low temperatures also increases the volume of material able to be a source in a given thermal regime.

The potency of the above proposition can be demonstrated. Usual thermal gradients correspond to magma depths of 3 to 10 km and to depths of ca. 0.3 to 1.5 km for 200° C. Hence ca. 2.5 to 8 km thickness of source material(s) may be above 200° C from which virtually all the adsorbed mercury can be liberated. For non-adsorbed mercury a higher temperature, say 350° (minimal), is required for the significant release of mercury; the corresponding source thicknesses are 2.0 to 6.5 km. Since the lateral thermal gradients are lower than the central vertical gradients the source volume

is reduced by more than 8^3 to 6.5^3 km^3; i.e. more than 50% (A minimum source volume for a 2 km source thickness is about 10 km^3, and for an 8 km cube the volume is 600 km^3).

The mercury concentrations in possible sources range from 0.025 ppm to 1 ppm, the corresponding volumes required to produce an average mercury deposit (ca. 1,500 tonne) are about 21.0 to 0.5 km^3 for 100% efficient deposition. By comparison with the deposition efficiency at Ngawha Springs the volumes are 450 km^3 and 11 km^3 respectively; for Almaden, the largest known deposit, 3,100 km^3 (14.6 $km)^3$ of a 0.5 ppm source would be required.

The above conditions for mercury production from a source and a given temperature regime imply that for very small deposits there is not necessarily a preferred source, except that mercury able to be released at low temperatures will considerably increase the effective volume of the source and hence the total mercury involved in a given hydrothermal system. For deposits where there is a limited amount of magma (which usually contains 0.02 - 0.2 ppm Hg), 10 km^3 of magma would hold 600 to ca. 6,000 tonnes of mercury which is sufficient to form a deposit; but at 5% efficiency for the economic deposition, the figures are reduced to 30 to 300 tonnes, smaller than commercial deposits. Hence at least 25 km^3 of magma needs to be present for deposits of 750 tonnes or more.

The presence of suitable country rock ($\geqslant$ 0.1 ppm Hg) increases the potential yield by over five fold that possible at Ngawha Springs; i.e. > 4,000 tonne. At least 85% of all mercury deposits are associated with sediments at the time of formation, many with thick sedimentary piles (e.g. $\geqslant$ 8 km stratigraphic thickness at Almaden (Saupé, 1973), and a large number are also associated with olistotromes or some other chaotic sedimentary assembly (e.g. The Franciscan Formation, The Northland Chaos Breccia and The Piedra Frialesca)).

Another possible point against magma as a major source for economic mercury deposition is that the higher temperatures cause more diffusion and larger dispersion of mercury in virtually all directions. Since a magma is probably not wholly inside a hydrothermal convection cell but only in partial 'contact' (on the upper side) with the hydrothermal convection system, the loss of mercury outside the convection system and hence 'ore-solutions' may well be significant, whereas mercury generated within the cooler circulating 'ore-fluids' is more likely to escape with the other volatiles in the hot spring/ore-fluid system.

A complementary factor in the mobilization of mercury is the release of other volatiles, especially gases. Since mercury is volatile it can be extracted more rapidly and completely from a source by gas via a process similar to steam distillation (as well as destructive distillation). Hence rocks with high volatile contents, such as organic materials, water and some carbonates may cause the early 'ore-fluids' to carry more mercury and speed-up/increase the early deposition of mercury near the surface. Similarly supercritical and gaseous fluids can also enhance mercury extraction.

c. The Transport Medium

The dominant and stable form of mercury at depth is the element due to the prevailing temperatures and Eh's (discussed in chapter two). Hence Hg^{o} is also the dominant form transported. In order to move the mercury in sufficiently large concentrations and quantities a miscible fluid is needed. However the properties of the fluid may change as it passes the critical temperature (Tc) during the upward passage. Commonly the mercury depositing fluids are dilute brines ($\leqslant$ 2%) with variable dissolved carbon dioxide (White, Hem and Waring, 1963; Waring, 1965; Barnes, 1967; Krauskopf, 1967; Roedder, 1972; Giggenbach and Lyons, 1977 and Ellis and Mahon, 1973) hence $265^{o} \leqslant Tc \leqslant 400^{o}C$.

Above the critical point everything is miscible, but below it there are gas and liquid phases, and the mercury strongly partions into the gas phase (Bonhoeffer and Reichart, 1931; Glew and Hames, 1971). The element also has a substantially greater solubility in natural waters than its sulphur complexes which above 200° decompose (Dickson, 1964 and 1976).

The gas phase can transport considerably more mercury metal than the liquid phase(s) if the phases are present in similar volumes: the ratios of concentrations of mercury in equal volumes of gas and aqueous solution at 25°, 100 and 120°C are ca. 500, 8000 and 11,000 respectively (Glew and Hames, 1971). Hence the presence of 1% gas with 'ore-solutions' considerably increases the movement (transport) of mercury. For example, close to the surface most 'ore-solutions' are about 50°C or more (White, 1967), thus the aqueous phase can hold at least 0.1 ppm, and with 1% gas the total fluid can carry over 1 ppm Hg^{o}; for 120° the total concentration is about 110 ppm.

Because large volumes of hot gas can carry abundant mercury, their direct escape into the atmosphere may cause a large proportion of the 'ore-solution' mercury to be lost. Hence an efficient deposition process, or even the deposition of any cinnabar, depends on how minimal the loss is. The fumarolic loss depends on the mercury

concentration and the flow rate. Mercury concentration, up to saturation depends on the gas temperature. The concentration or vapour pressure of mercury approximately doubles every ten degrees between 10 and 100°C, so temperature is a very potent parameter. Consequently the cooler the escaping gases, the more mercury is left to form the deposit. This is favoured by a steep geothermal gradient and relatively cool surface conditions. (Too low a near-surface temperature may inhibit the kinetics of some cinnabar forming mechanisms).

A low gas flow or escape for a given amount of transported mercury requires a high concentration of mercury to be present in the deep fluid. The main limit is that there be sufficient gas to transport the mercury available and that the concentration is realistic (25 to 800 μg/l is the concentration range at Ngawha Springs).

For many deposits the mercury concentrations in associated fluids without a separate gas phase are below 0.1 ppm, which possibly means that sufficient transport of elemental mercury can take place in the aqueous phase alone. (Even so the thermodynamic conditions and the concentrations do not support reduced sulphur complexes). Notably Hg^{o} has been detected at many springs and it is more than adequately soluble all the waters (White, 1967; Dickson and Tunell, 1968; Davey and van Moort, 1974). The lack of gas flow in most of the springs has probably allowed the deposition of cinnabar, for even a modest gas flow would carry off 99% of the mercury. Without gas the loss of mercury due to high exhalation temperatures is very small, hence near boiling-point springs depositing cinnabar are more feasible at low mercury concentrations where a gas phase is absent.

A further enhancement of deposition efficiency may occur where a maximum mercury concentration (and quantity) enters the deposition zone in the aqueous phase. (It is anticipated that maximum aqueous mercury concentrations may increase the kinetic rate(s) of deposition). This is also favoured by minimal gas phase separation from the aqueous phase, and if gas is present by minimal surface temperatures also. In a relatively gaseous system the optimum conditions could be met by the hydrothermal fluids encountering 'cold' water.

(For instance at Ngawha Springs, if the fluid composition (gas to liquid ratio) for the most efficient deposition of cinnabar were delivered into the deposition environment, and the mercury reacted in proportion to its aqueous concentration, there would be 100% more cinnabar. Temperatures in the deposition regions are up to 92°C, whereas the mercury only saturates the fluids up to ca. 75°C. Increasing the mercury concentration and decreasing the proportion of gas in the total fluid to yield

mercury saturation up to ca. 92°C and maintaining a constant mercury flux reduces the gas by 70%. This causes the aqueous concentration of mercury to double, and at unchanged surface temperatures the amount of mercury condensed from the escaping gas increases by a negligible amount).

d. Deposition Medium

Deposition media cover a wide range of lithologies (Dreyer, 1940), and in a large number of deposits cinnabar has not reacted with the host. Most media have had or have a large degree of porosity and permeability to fluids. (The porosity may be cogenetic or due to brecciation, fractures, weathering, alteration and dissolution). Some deposits are entirely superficial; e.g. sinter and fluvial sediment hosts. Hence the deposition medium is probably a physical rather than chemical host; however, it is a site for chemical reactions between other components.

The majority of host media were relatively superficial during deposition, and show signs of hydrothermal activity. (Some important rare exceptions are New Almaden, Geysers and possibly the Almaden, where cinnabar has been found at depths up to 610 to 1800 m (Weisberg, 1975). At Almaden at least some of the deposition environment was probably superficial at the time of cinnabar deposition (Park, 1970; Saupé, 1973 and 1976). If the few deposits which are deep (> 250 m) form by an oxidation mechanism, then oxidizing water must be able to reach the deposition environment: this can be possible (e.g. Meyer, 1975). Such a requirement is unlikely to be fulfilled normally because a considerable permeability to descending water is required as well as a lack of reaction with its oxygen. Near surface environments permeable to oxygen/oxidizing waters are the most favoured.

A limit to the depth of deposition is the presence of a water-table. The table is a barrier to descending (oxygenated) water, and hence cinnabar deposition (c.f. Sulphur Banks in White and Roberson (1962)). Nevertheless water is needed as a solvent for the reactants (Hg, H_2S, O_2 and H^+), therefore major cinnabar deposition is restricted to wet environments. The presence of H_2S and oxygen in water causes sulphate to form which increases the acidity of the solutions which may cause extensive alteration of the host in the deposition environment. The alteration should decrease rapidly below the water table/sulphate-rich waters, where a different type of alteration could be present around fissures due to hydrothermal fluids. The zone of possible acid alteration is also the most favoured cinnabar deposition site because H^+, O_2, and H_2S are also about optimum for mercury oxidation and hence cinnabar deposition.

To maximize reaction rates and minimize dispersion, concentrations need to be maximal and the deposition should occur in relatively confined space(s). (The volume of ore plus sub-ore is usually small, ca. $\leqslant 10^{-4}$ km^3 or $(50\ m)^3$, although the largest deposit Almaden, occupies ca. 1.25×10^{-2} km^3 or $(230\ m)^3$ (calculated from Saupé, 1973)). Since the deposits are most likely to have occupied a superficial host, there is a strong possibility that erosion may seriously deplete the deposits. For deposits like those at Ngawha Springs, the richest parts of the deposit are most vulnerable. Hence deposits are unlikely to form or persist on/in ground which suffers significant erosion. Deposits thus favour flat and gently undulating ground without rapidly moving water(s).

Due to thermal decomposition of cinnabar in solutions above 200°C, the cooling of solutions from much higher temperatures certainly inhibits cinnabar formation and deposition until the temperature is below 200°C. Hence the depth of deposition in the geothermal gradients of ca. 100 - 500°C/km commonly present at deposition sites is limited to maximum depths of 400 to 2000 m. For boiling springs the maximum depth is ca. 1000m. In general deposition depths are likely to be much nearer to the surface to allow oxygen permeation.

e. Oxygen

The only viable source is the atmosphere. Oxygen is a gas soluble in water (ca. 2.5×10^{-4} M at 25°C P_{air} = 1 atm), hence it may diffuse and be transported in water. At Ngawha, reaction rates show that rain, streams and ground-water bring in oxygen. Rain and streams deliver by far most of the oxygen and are responsible for the richest cinnabar occurrences. The presence of chloride catalyses the continuous and slower rates of mercury oxidation found in waters with low oxygen concentrations.

For effective oxidation rates pH needs to be neutral to acid and the presence of dissolved chloride is desirable. The presence of both oxygen and hydrogen sulphide tends to ensure suitable pH's in the deposition region. Thermodynamic data for average hot springs depositing cinnabar indicate that the oxidation of mercury at pH = 5 is 'thermodynamically spontaneous' for oxygen concentrations above 10^{-19} M. At this order of concentration reactions would be slow. By comparison with Ngawha Springs, where Eh $\approx$ -0.5 and pH $\approx$ 5 in regions depositing economic to subeconomic concentrations of cinnabar, a more practical limit is a minimum of 10^{-8} M O_2 (3 ppb) or about 10^{-5} times the oxygen concentration in air-saturated water at 25°C.

The main barriers to oxygen are permeability, depth and reducing conditions.

The presence of a water-saturated environment commonly blocks the penetration of oxygen unless the water is descending. Once water has mixed with hydrothermal fluids below the surface, the water is usually reducing and thus inhibits mercury oxidation. Deep surface waters may also have relatively reducing conditions at the bottom due biotic oxygen consumption. Hence the proposed cinnabar deposition mechanisms are most unlikely to occur in oceans and deep lakes. Boiling is another probable inhibitor of oxidation, since degassing occurs with boiling, hence a large proportion of any dissolved oxygen would be removed.

Oxidation-wise the surface few metres are optimum for cinnabar deposition. For oxygen to penetrate over 500 m deep, very water permeable rock is needed: e.g. porous sandstones, breccias and heavily jointed rocks.

f. Water

Water is present in all geothermal systems, and it is the vehicle for the deposition reactions. The liquid is essential to the mechanisms. Water at the deposition sites may consist of ground-water, rain, streams, pools and geothermal water. The only problems which could arise are most unlikely: excessive temperatures and too little water.

Very hot fumaroles could prevent the presence of (sufficient) water at otherwise suitable deposition sites. (Steam would also co-exhaust the bulk of the mercury, hydrogen sulphide and oxygen). Excessively cold conditions might also inhibit cinnabar deposition, ground covered in ice could block the entry of oxygen into potential deposition sites. Generally it is anticipated that ice should melt in the presence of thermal emissions. The likelihood of a dry climate causing the absence of (suciffient) water is remote. Most thermal systems can supply enough water to cause at least water-saturated ground. The most likely of the set of possible deposition inhibitors is the combination of excessively hot geothermal emissions in a dry climate.

Probably the main difficulty which relates directly to water is that in a very low rainfall area there could be a lack of surface water(s) to supply oxygen to the deposition environment.

g. Sulphur

The form of sulphur required for cinnabar to deposit is the '-2' valence state species in aqueous solution. The sulphur can be supplied from a variety of sources depending on temperature, Eh, pH and the presence of certain bacteria. The source can be various sulphides and sulphates and possibly elemental sulphur (All are known sources, except that the only known reactions involving elemental sulphur do not give rise to significant quantities of cinnabar (White, 1976)).

The abundance of sulphur relative to mercury is two to four orders of magnitude greater in most rocks (Wedepohl, 1972), hence the concentration of sulphur is unlikely to be so low as to prevent cinnabar deposition in most geothermal systems. The source may be the same as for mercury or different.

(For instance at Ngawha, isotope data suggest that the H_2S is compatable with a magmatic origin, whereas mercury most likely comes from a sedimentary source). Because mercury deposits are associated with abnormally high temperatures near the surface (White, 1967) and because 'deep' geothermal conditions are normally reducing, it is likely that a significant amount of the sulphur supplied to deposition sites (before oxidation) is hydrogen sulphide, so that sulphate reduction is not normally required.

Whatever the source, (some) H_2S almost invariably ascends with the geothermal fluids, and therefore (as with water) is not usually a serious limiting factor to mercury deposition as it could be for the much larger massive sulphide deposits.

h. The optima for economic mercury deposition are thus:-

i Large non-metomorphic bodies of marine sediments in a feasible source position.

ii Areas (of, or adjacent to tectonism) with a steep geothermal gradient.

iii Dominantly subaerial ground (with little or no erosion and no steep slopes for superficial deposits).

iv Hot springs with at least minor associated volatiles.

v Oxygenated water available to mix with geothermal fluids.

vi Country rocks permeable to oxygenated and geothermal fluids.

vii $pH < 8$.

viii Dissolved sulphide is readily available.

ix The area around the deposition site and the geothermal plumbing is impermeable to mercury.

Optima for preserving the deposits are:-

x Gas flow and heat anomalies cease soon after mercury deposition has terminated. (Includes no temperature metamorphism of the deposit).

xi Burial or capping of the deposit by mercury impermeable rock which also prevents the entry of aerated waters and ferric ions.

(11.4) SOME APPLICATIONS OF THE MODEL AND MECHANISMS

Uses to which the model and mechanisms for cinnabar deposition may be put are the prospecting and extraction of mercury, geothermal energy detection and pollution abatement. Mercury may be found more efficiently by limiting searches to areas which fulfil the criteria set down in sections (11.3) and (2.4). Within the appropriate areas it could be possible to extract mercury by the direct cooling of geothermal fluids to condense the mercury if there is current transport of mercury in the vapour phase.

Because the model requires a steep thermal gradient, then where there are current or recent large mercury anomalies it is likely that there is steam relatively near the surface which possibly could be used for energy production. Furthermore there is the possibility that the flux of mercury from area (or the concentration in fluids) could be used to give an estimate of the geothermal energy output.

Under suitable conditions the filamentous bacteria may be used to significantly reduce mercury levels in water and sediments (e.g. 'oxidised' water could be passed through a bed of coal ash, vegetation waste and/or sand plus gypsum or some other slightly soluble sulphate). As the Hg^{2+} and $SO_4^{=}$ containing water passes through the vegetation, the bacteria reduce $SO_4^{=}$ to $S^{=}$ and the mercury is fixed as insoluble cinnabar along with most other heavy metals. Other ways of taking the mercury out of solution using the deposition mechanisms are also possible, but the above is probably the most viable (and cheapest.)

Prospecting for mercury deposits which form by the mechanisms developed needs to be in subaerial areas with high heat anomalies and a sufficient quantity of sedimentary rocks available for the mercury source ($\geqslant 5\ km^3$). The other deposition criteria are less likely to be useful except if a region is already known not to satisfy them. Highly mountainous terrain is unlikely to have deposits form although there could be old deposits. Areas which have undergone medium to high temperature metamorphism since possible ore deposition are also unlikely to contain any cinnabar deposits.

(11.5) SUMMARY

The deposition and attrition mechanisms for the Ngawha deposits (which are closely compatable with many other mercury deposits) yield explanations for the traits of mercury deposits. Nearly all the traits are inherent in the mechanisms developed for Ngawha; Similarly means for more efficient mercury exploration result, as well as applications for pollution abatement and geothermal anomaly detection.

(11.6) CRITICISM OF THE MODEL

i. A major criticism was that the mercury in the vapour phase at Ngawha possibly comes from the dissociation of the local cinnabar.

Answer

The mercury is present in high concentrations in hot gases below the cinnabar depositing region, and is present in gas ($> 1\ \mu g/l$) from NG1 which is over 500 m deep and 1 km from the hot springs and the cinnabar deposits. The vapour pressure of mercury from cinnabar dissociation is also far too small to account for a significant contribution in the hot gases, for where there is cinnabar the temperatures are below 100° C.

ii. At depth solutions are more alkaline and therefore can carry more HgS.

Answer

At Ngawha, although the solutions are more alkaline at depth and even if no thermal decomposition of mercury species occurred, the solutions still could not transport enough mercury to account for the quantity found in the near-surface fluids. Apart from the problems of insufficient alkalinity, sulphur and water flow, aqueous solutions of mercury-sulphide complexes decompose appreciably above 200° C and yield elemental mercury. Therefore at higher temperatures ($\geq$ 236° C) no sulphur complexes could exist let alone be formed. Worse if a passing gas phase is present even solutions below 200° C may also entirely decompose as the metal is taken away by the gas. Hence at Ngawha one would expect any alkaline sulphide complexes (even if they could form) to entirely dissociate.

iii. There is no known oxidizing agent (in nature) capable of oxidizing Hg^{o} to Hg^{2+}.

Answer

The mechanism presented for oxidation was observed in the field, proved to work in the laboratory on both natural and synthetic solutions. Reaction potentials also imply that the reaction mechanism is thermodynamically spontaneous. (Other more oxidizing potentials are also known in nature: e.g. for crocoite and pyrolusite. Hence similar oxidizing agents do exist in nature, and not just at Ngawha Springs.

BIBLIOGRAPHY

Aidin'yan, N.Kh., 1962: Content of mercury in some natural waters. Akad. Nauk S.S.S.R. Trudy Inst. Geol. Rudn. Mestorozhd., Petrog., Mineral., Geokhim., 70, 9-14; Chem. Abs., 57, 16336 (1962).

Aidin'yan, N.Kh., 1966: Some genetic features in the formation of mercury-containing mineralization from the study of contemporary volcanism. Acad. Nauk. S.S.S.R., Inst. Geol. Rudn. Mestorozhd., Petrog., Mineral., Geokhim., Ocherki Geokhim. Endagenn. i Gipergenn. Protsessov, 87-92.

Aidin'yan, N.Kh. and Ozerova, N.A., 1968: Geochemistry of mercury. Problemy Geokhim. Kosmol., 160-165; Chem. Abs., 70 (7), 143.

Aidin'yan, N.Kh., Troitskii, A.I. and Balavshaya, G.A., 1964: Distribution of mercury in various soils of the U.S.S.R. and Vietnam. Geochimiya, 654-659.

Anderson, A., 1967: Kvicksilvert i Marken. Grundforblattring, 20 (3-4), 95-105.

Andren, A.W. and Harriss, R.C., 1973: Methylmercury in estuarine sediments. Nature, 245.

Baev, V.G., 1968: Distribution of mercury in natural waters of the southern slopes of northwestern Caucasus. Akad. Nauk S.S.S.R. Dodlady, 181, 1249-1251.

Bailey, E.H., 1959: Froth veins formed by immiscible hydrothermal fluids in mercury deposits, California. Bull. Geol. Soc. Am., 70, 661-664.

Bailey, E.H., 1961: Chemical analyses of brines and crude oil, Cymric Oil Field, Kern County, California. U.S.G.S. Prof. Paper 424-D, D306-309.

Bailey, E.H. and Everhardt, D.L., 1964: Geology of the quicksilver deposits of the New Almaden District, Santa Clara County, California. U.S.G.S. Prof. Paper 360, 206p.

Bailey, E.H., Snavely, P.D. and White, D.E., 1961: Chemical analyses of brines and crude oil, Cymric Oil Field, Kern County, California. U.S.G.S. Prof. Paper 424-D, D306-309.

Bailey, E.H. and Vitaliano, D., 1979: The metallogeny of mercury. (Review) Econ. Geol., 74, 166-168.

Ballance, P.F., 1974: An inter-arc flysch basin in northern New Zealand: Waitemata Group (Upper Oligocene to Lower Miocene). J. Geol., 82, 437-471.

Ballance, 1975: Evolution of the India-Pacific plate boundary in North Island, New Zealand. Bull. Aust. Soc. Explor. Geophys., 6, (2 part 3), 57-58.

Ballance, P.F., 1976: Evolution of the Upper Cenozoic magmatic arc and plate boundary in northern New Zealand. Earth and Planet. Sci., 28, 356-370.

Bannikova, L.A., Sushchevskaya, T.M. and Volkov, B.I., 1975: Chemical composition and complexing in solutions which had formed the cinnabar of the North-Western Caucasus. Geochimiya, 5, 715-726.

Banwell, C.J., 1965: Geophysics, p.38-41. In Thompson and Kermode (eds.), 1965.

Barber, J., Beauford, W. and Shieh, Y.J., 1974: Some aspects of mercury uptake by plant, algal and bacterial systems in relation to its biotransformation and volatilization in mercury, mercurials and mercaptans. Eds. Miller and Clarkson, 4th Rochester Conf. on Environmental Toxicology, 1971. Charles C. Thomas, Springfield, Illinois.

Barnes, H.L., 1967: Geochemistry of Hydrothermal Ore Deposits. Holt, Rinehart and Winston, Inc., New York. 670p.

Barnes, H.L. Romberger, S.B. and Stemprok, M., 1967: Ore solution geochemistry. II. Solubility of HgS sulphide solutions. Econ. Geol., 62, 957-982.

Barnes, I., 1970: Metamorphic waters from the Pacific tectonic belt of the west coast of the United States. Science, 168, 973-975.

Barnes, I., 1977: Oral communication and in Giggenbach and Lyon, 1977.

Barnes, I., Hinkle, M.E., Rapp, J.B., Heropoulos, C. and Vaughn, W.W., 1973: Chemical composition of naturally occurring fluids in relation to mercury deposits in part of north-central California. U.S.G.S. Bull. 1382-A.

Barnes,, I., Irwin, W.P. and Gibson, H.A., 1975: Geologic map showing springs rich in carbon dioxide and chloride in California. U.S.G.S. Water Resources Investigations.

Barringer, A.R., 1972: Exploration Geochemistry. Barringer Research, 49p. (Authors for the article are Bradshaw, Clews and Walker).

Bell, J.M. and Clarke, E. de C., 1909: The geology of the Whangaroa subdivision, Hokoanga division, New Zealand. N. Z. Geol. Surv. Bull., 8.

Blattner, P., 1978: oral communication.

Bloom, H., 1975: Heavy metals in the Derwent estuary. Chem. Dept., Univ. of Tasmania, (September), 121p.

Boer , J.R., 1944: The behaviour of mercury compounds in soils. Ann. Appl. Biol., 31, 340.

Bonhoeffer, K.F. and Reichart, H., 1931: Zeitsch. Phys., 67, 780.

Bowen, F.E., 1966: Ngawha Springs. New Zld. Geol. Surv. Rept. 16, 25-31 and 35.

Bradshaw, P.M.D., and Koksoy, M., 1968: Primary dispersion of mercury from cinnabar and stibnite deposits, W. Turkey. 13th Int. Geol. Congr., 7, 341-355.

Brandenberg, H. and Bader, H., 1965: The determination of mercury by flameless atomic absorption. II. A static vapour method. Atomic Abs. Newsl., 7, 53-54.

Brothers, R.N., 1965: In Thompson and Kermode (eds.), 1965, 33-37.

Brothers, R.N., 1974: Kaikoura Orogeny in Northland, New Zealand. New Zld. J. Geol. Geophys., 17, 1-18.

Burkstaller, J.E., McCarty, P.L. and Parks, G.A., 1975: Oxidation of cinnabar by Fe (III) in acid mine waters. Environ. Sci. and Technol., 9, 676-678.

Carr, R.A., Jones, M.M. and Russ, E.R., 1974: Anomalous mercury in near bottom water of a mid-Atlantic rift valley. Nature, 251, 987-988.

Dall'Aglio, M., 1968: The abundance of mercury in 300 natural water samples from Tuscany and Latium (Italy). In "Origin and Distribution of the Elements." Internat. Earth Sci. Ser. Mon., 30, 1065-1081.

Davey, H.A., 1974: Mechanism for mercury deposition at Ngawha Springs, New Zealand. Pap. Proc. roy. Soc. Tasm., 108, 157-158.

Davey, H.A., 1976: Present mercury deposition at Ngawha Springs, New Zealand. 25th Int. Geol. Congr., 1, 210.

Davey, H.A., 1977: Economic cinnabar deposition from bacterial reduction and oxidation of thermal spring water. In "Abstracts of the Carey Appreciation Symposium", Univ. of Tasmania, Feb. 1977, 46.

Davey, H.A. and van Moort, J.C., 1974: Current mercury deposition at Ngawha Springs, New Zealand. Search, 5 (4), 154-156.

Dickson, F.W., 1968: The origin of mercury haloes. 13th Int. Geol. Congr., 7, 357-265.

Dickson, F.W., 1964: Solubility of cinnabar in Na_2S solutions at 50-250°C and 1-1800 bars, with geologic applications. Econ. Geol., 59, 625-635.

Dickson, F.W., 1976: oral communication.

Dickson, F.W. and Tunnell, ., 1968: Mercury and antimony deposits associated with active hot springs in the United States. In "Ore deposits of the United States, 1933-1967", 2, ch.80, 1673-1701. The Am. Inst. of Min. Met. and Pet. Eng., New York.

Dreyer, R.M., 1940: The geochemistry of quicksilver mineralization. I & II. Econ. Geol., 35, 17-48 and 140-157.

Dvornikov, R.G., 1967: The distribution of mercury in anthracites of the Bokovo-Khrustalnaya Basin (Donbass). Acad. Nauk R.S.R. Dopovidi, Ser.B, 29, 293-298; Chem. Abs., 56, 5298.

Ehmann, W.D. and Lovering, J.F., 1967: The abundance of mercury in meteorites and rocks by neutron activation analysis. Geochim. et Cosmochim. Acta, 31, 357-376.

Ellis, A.J., 1970: Quantitative interpretation of chemical characteristics of hydrothermal systems. Geothermics, 2 (1), 516-528.

Ellis, A.J. and Mahon, W.A.J., 1966: Geochemistry of the Ngawha hydrothermal area. New Zld. J. Sci., 9 (2), 440-456.

Ellis, A.J. and Mahon, W.A.J., 1973: Chemistry and Geothermal Systems. Academic Press, New York. (Ed. J. Denton).

Eshleman, A., Siegel, S.M. and Siegel, B.Z., 1971: Is mercury from Hawaiian volcanoes a natural source of pollution? Nature, 233, 471-472.

Fedorchuk, V.P., 1963: Some problems on the origin of mercury-antimony deposits. In symposium "Problems of Postmagmatic Ore Deposition", Prague 1963, Appendix to vol.1. Czech. Geol. Surv., 87-90.

Fedorchuk, V.P., 1974: In Bailey, E.H. and Cammarota, V.A., 1975, International Mercury Congress. World Mining, 28, 45-47.

Fedorchuk, V.P., Kostyleva, E.E. and Maslova, I.N., 1963: Some problems of the genesis of mercury-antimony deposits. Geol. Rudn. Mestorozdh., 5 (9), 91-99.

Fleischer, M., 1970: Summary of the literature on the inorganic chemistry of mercury. U.S.G.S. Prof. Paper 713, 6-13.

Fleming, C.A., 1945: Hydrothermal activity at Ngawha, North Auckland. New Zld. J. Sci. and Tech., 26, 255-276.

Friedrick, G.H. and Hawkes, H.E., 1966: Mercury dispersion haloes as ore guides for massive sulphide deposits, West Shasta District, California. Mineral. Deposita, 1, 77-88.

Frissel, M.J., Poelstra, P. and van der Klugh, N., 1974: The contamination of Dutch soils with mercury and a few other heavy metals. Geol. en Mijnbouw, 53 (4), 163-170.

Garrels, M.R. and Christ, C.L., 1965: Solutions, Minerals and Equilibria. Harper and Row, New York.

Gatehouse, S., 1973: The Geochemistry of Mercury. Honours reading thesis, Geology Dept., Univ. of Tasmania.

Gavis, J. and Ferguson, J.F., 1972: The cycling of mercury through the environment. Water Research, 6, 989-1008.

Giggenbach, W. and Lyon, G.L., 1977: The chemical and isotopic composition of water and gas discharges from the Ngawha geothermal field, Northland. New Zld. D.S.I.R. Geothermal Circular CD:30/555/7-WFG and I.N.S. Contribution no.89, 37p.

Glew, D.N. and Hames, D.A., 1971: Aqueous nonelectrolyte solutions, Part X. Mercury solubility. Can. J. of Chem., 49, 3114-3122.

Golonya, S.V. and Volobeyev, M.I., 1970: Distribution of mercury in granitic rocks of the Yenisei Range. Geochimiya, 256-261.

Gough, R.P., 1965: Kaikohe, Sheet N15 of the 1:63,360 map series. N.Z.M.S.1.

'Grasslands', 1975: oral communication with officers of the Agricultural Division of the New Zealand D.S.I.R. at Kaikohe.

Griffiths, A.P., 1898: The Ohaeowai quicksilver deposits. Trans. N.Z. Inst. Min. Eng., 2, 48-60.

Griffiths, J.R., 1973: Tectonic History of the South-west Pacific Region. Two volumes of Ph.D. thesis, Univ. of Tasmania.

Gustafson, L.B. and Hunt, J.P., 1975: The porphyry copper deposit at El Salvador, Chile. Econ. Geol., 70 (5), 857-912.

Hatch, W.R. and Ott, W.L., 1968: Determinations of sub-microgram quantities of mercury by atomic absorption spectrophotometry. Analyt. Chem., 40 (14), 2085-2087.

Healy, J., 1945: Underground water at Ngawha. New Zld. J. Sci. and Technol., 26, 273-276.

Healy, J., Skinner, D.N.B. and Bowen, F.E., 1966: Ngawha geothermal area, Northland. New Zld. Geol. Surv. Rept. 16, 35 and 25-26 (drillhole log).

Heide, F., Lerz, H. and Bohm, G., 1957: Content of lead and mercury in the Saale. Naturwissenschaf., 16, 441-442.

Hem, J.D., 1970: Chemical behaviour of mercury in aqueous media. U.S.G.S. Prof. Paper 713, 19-24.

Henderson, J., 1944: Cinnabar at Puhipuhi and Ngawha, North Auckland. New Zld. J. Sci. and Technol., 26, B47-59.

Hinkle, M.E. amd Learned, R.E., 1969: Determination of mercury in natural waters by collection on silver screens. U.S.G.S. Prof. Paper 650-D, 251-254.

Hoggins, F.E., 1972: Analytical and Geochemical Studies of Mercury. M.Sc. thesis, Chemistry Dept., Massey Univ., New Zealand.

Hoggins, F.E. and Brooks, R.R., 1973: Natural dispersion of mercury from Puhipuhi, Northland, New Zealand. New Zld. J. of Marine and Freshwater Res., 7, 125-132.

Hornibrook, N. de B., Scott, G.H. and Edwards, A.R., 1966: Ngawha geothermal area, Northland. New Zld. Geol. Surv. Rept. 16, 23-24.

Hosoharam K., Kozuma, H., Kawasaki, K. and Tsuruta, T., 1961: Total mercury content of sea-water. Nippon Zasshi, 82, 1479-1480. Chem. Abs., 56, 5766.

Ingham, C.E., 1965: Magnetic Survey; "Vulcanology". New Zld. D.S.I.R., Inf. Series 49, 43-45.

James, R.D. and MacNaughton, ., 1977: The adsorption of aqueous heavy metals on inorganic minerals. Geochim. et Cosmochim. Acta, 41 (11), 1549-1556.

Jenne, E.A., 1970: Atmospheric and fluvial transport of mercury. U.S.G.S. Prof. Paper 713, 40-45.

Jensen, S. and Jernelov, A., 1969: Biological methylation of mercury in aquatic organisms. Nature, 223, 753-754.

Jonasson, I.R., 1970: Mercury in the environment, a review of recent work. Geol. Surv. Canada paper 70-75.

Jones, W.M., 1939: Magnetic effects associated with cinnabar deposits, Ngawha, North Auckland. New Zld. J. Sci. and Technol., 20, B272-276.

Jovanic, S. and Reed, G.W., 1968: Mercury in metamorphic rocks. Geochim. et Cosmochim. Acta, 32, 341-346.

Karasik, M.A., Goncharov, Yu.I. and Vasilev'skaya, A.E., 1965: Mercury in mineralized waters and brines from the Permian Halogen Formations in the Donets Basin. Geochimiya, 117-121.

Kear, D., 1961: Relative ages, structure and sequence of Kerikeri Basalts in Bay of Islands volcanic zone, Appendix 1, in Bauxite deposits in Northland. D.S.I.R. Inf. Series, 32, 12-39.

Kear, D., 1964: Volcanic alignments north and west of New Zealand's central volcanic region. New Zld. J. Geol. and Geophys., 7, 24-44.

Kear, D., 1966: Ngawha Springs. New Zld. Geol. Surv. Rept. 16, 2 and 32-35.

Kear, D. and Hay, R.F., 1961: North Cape. Edn. 1 of Sheet 1 "Geological Map of New Zealand 1:250,000." D.S.I.R., Wellington.

Kear, D. and Thompson, B.M., 1964: Volcanic risk in Northland. New Zld. J. Geol. and Geophys., 7, 87-93.

Kear, D. and Waterhouse, B.C., 1967: The Onerahi Chaos Breccia. New Zld. J. Geol. and Geophys., 10 (3), 629-646.

Khodakovsky, I.L., Popova, M.Ya. and Ozerova, N.A., 1975: On the role of sulphide complexes in the transfer of mercury by hydrothermal solutions. Geokhimiya, 3, 360-370.

Klusman, R.W., and Landress, R.A., 1978: Secondary controls on mercury in soils of geothermal areas. J. Geochem. Explor., 9, 75-91.

Knox, J., 1906: Zur Kenntnis Der Ionenbildungen Des Schwefels und Der Komplexionen Des Queckselbers. Zeitschr. Elektrochemie, 12, 477-481.

Kokot, M.L., 1974: A review of the methods for the determination of mercury in geological samples by flameless atomic-absorption spectrophotometry. Mins. Sci. and Engng., 6 (4), 236-244.

Koksoy, M. and Bradshaw, P.M.D., 1969: Secondary dispersion of mercury from cinnabar and stibnite deposits, west Turkey. Col. Sch. Mines Quart., 64, 333.

Koksoy, M., Bradshaw, P.M.D. and Tooms, J.S., 1967: Notes on the determination of mercury in geological samples. Inst. Min. Met. Trans. Bull., 76, B121.

Kothny, E.L., 1973: Three phase equilibrium of mercury in nature. Am. Chem. Soc. "Trace Elements in the Environment." Advances in Chem. Series 123, ch.4, 48-80.

Krainov, S.R., Volkov, G.A. and Korol'kova, M.Kh., 1966: Distribution and mode of migration of the trace elements Zn, Cu, Hg, Li, Rb, Cs, As and Ge. Geokhimiya, 180-196.

Krauskopf, K.B., 1951: Physical chemistry of quicksilver transport in vein fluids. Econ. Geol., 59, 498-523.

Krauskopf, K.B., 1956a: The possible role of volatile metal compounds in ore genesis. Econ. Geol., 59, 22-45.

Krauskopf, K.B., 1956b: Factors controlling the concentration of thirteen rare metals in sea-water. Geochim. et Cosmochim. Acta, 9, 1-32B.

Krenkel, P.A., 1973: Mercury: Environmental Considerations, Part I. C.R.C. Critical Reviews in Environmental Control, 303-373. (published with volume two: Krenkel, 1974).

Krenkel, P.A., 1974: Mercury: Environmental Considerations. Part II. C.R.C. Reviews in Environmental Control., 251-339.

Kvashnevskaya, N.V. and Shablovskaya, E.I., 1963: Study of the contents of ore elements in the suspended matter of river systems. Akad. Nauk, S.S.S.R. Doklady, 151, 426.

Leckie, J.O. and James, R.O., 1974: Control mechanism for trace metals in natural waters. In "Aqueous Environment Chemistry of Metals." (Ed. A.J. Rubin), ch.1, 1-75. Ann Arbor Science Publishers Inc.

Leitch, E.C., 1975: Mesozoic-Middle Tertiary tectonic development of northern New Zealand. Bull. Aust. Soc. Explor. Geophys., 6 (2 part 3), 56-57.

Lindberg, S., 1973: Thesis, Florida State Univ. In Andren and Harris, 1973.

Livingston, D.A., 1963: Chemical composition of rivers and lakes. U.S.G.S. Prof. Paper 440-G.

Long, S.J., Scott, D.R. and Thompson, R.J., 1973: Atomic absorption determination of elemental mercury collected from ambient air on silver wool. Anal. Chem., 45 (13), 2227-2233.

Loring, D.H. and Bremers, J.M., 1978: Geochemical mass balances for mercury in a Canadian fjord. Chem. Geol., 22, 309-330.

Low, H.V., 1974: Mercury: The Distribution and Measurements of its Isotopes. Honours thesis, Chemistry Dept., Univ. of Tasmania.

Lu, F.C., Berteau, P.E. and Clegg, D.J., 1972: The Toxicity of Mercury in Man and Animals. Int. Atomic Energy Agency, Vienna. Tech. Repts. Series, 137. "Mercury Contamination in Man and His Environment." ch.6, 67-85.

Lyon, G.L., 1977: Ngawha hot springs. Progress report of Inst. of Nuclear Sciences, 50/121/-GLL.

Lyon, G.L., 1978: written communications.

MacNaughton, M.G. and James, R.O., 1974: Adsorption of aqueous mercury. II. Complexes at the oxide/water interface. J. of Colloid and Interface Sci., 47 (2), 431-440.

Marovski, G. and Wedepohl, K.H., 1972: General trends in the behaviour of Cd, Hg, Tl and Bi in some major rock forming processes. Geochim. Cosmochim. Acta, 35, 1255.

Maslova, I.N., 1963: Ultramicrochemical study of the composition of solutions in quartz of antimony-mercury deposits. Vses. Mineral. Obshch. Zap., 92, 706-707.

Matlick, J.S. and Buseck, P.R., 1976: Exploration for Geothermal Areas Using Mercury - A New Geochemical Technique. Proc. 2nd U.N. Symposium on the Development and Use of Geothermal Resources, San Francisco, 1, 785-792.

McCarty, J.H., Meuschke, J.L., Ficklin, W.H. and Learned, R.E., 1970: Mercury in the atmosphere. U.S.G.S. Prof. Paper 713, 37-39.

McCarty, J.H., Vaughn, W.W., Learned, R.E. and Meuschke, J.L., 1969: Mercury in soil-gas and air. A potential tool in mineral exploration. U.S.G.S. Circ. 609, 16p.

McDonald, D.C., 1966: Hydrogen and oxygen isotope ratios in the waters of the Ngawha hydrothermal area, North Auckland. Bull. Vulcanologique, 29, 691-708.

McKeown, M.R., 1953: Coal in Australia. 5th Empire Min. and Metall. Congr., Aust. and N.Z., 4, 832p.

McNerney, J.J. and Buseck, P.R., 1973: Geochemical exploration using mercury vapour. Econ. Geol., 68, 1313-1320.

Meyer, C., 1975: erratum, see Gustafson, L.B. and Hunt, J.P., 1975.

Moiseyev, A.N., 1971: A non-magmatic source for mercury ore deposits? Econ. Geol., 66, 591-601.

Mulheim, M., 1973: Volcanic Geology of the Kaikohe Area. M.Sc. thesis, Geology Dept., University of Auckland, New Zealand.

Mulliken, R.S., 1976: Science is honest (interview). Chem. in Britain, 12 (3), 96097.

Murdock, J., 1967: Pendletonite, a new hydrocarbon from California. Am. Mineral., 52, 611-616.

Neville, G.A., 1967: The toxicity of mercury vapour. Can. Chem. Ed., 3 (1), 4-7.

Nier, A.O., 1950: A redetermination of the relative abundances of the isotopes of neon, krypton, rubidium, xenon and mercury. Phys. Rev., 79 (3), 450-454.

Ohta, N. and Terai, M., 1971: The mercury content of several acid hot springs in Japan. Bull. Chem. Soc. Japan, 44, 1153-1154.

Ozerova, N.A., 1962: Primary aureoles of dispersion of mercury. Akad. Nauk S.S.S.R. Trudy Inst. Geol. Rudn. Mestorozhd., Petrog., Mineral., Geokhim., (Transactions of the Institute for the Geology, Petrography, Mineralogy and Geochemistry of Ore Deposits), 72, 1-135.

Ozerova, N.A., 1973: Essays on the geochemistry of the volatile elements. Akad. Nauk S.S.S.R. Moscow (State Publishing House). Izdatelistvo 'Nauk'.

Ozerova, N.A., 1978: Mercury degassing ground. Doklady Acad. Sci. U.S.S.R., 239, (2), 450-453.

Ozerova, N.A. and Aidin'yan, N.Kh., 1966a: Distribution of mercury in sedimentary rocks. Litol i Polezn Iskop., 3, 49-57.

Ozerova, N.A. and Aidin'yan, N.Kh., 1966b: Mercury in sedimentary processes. Akad. Nauk S.S.S.R., Inst. Geol. Rudn. Mestorozhd., Petrog., Mineral., Geokhim., Ocherk Geokhim. Endogenn. i Gipergenn. Protessov, 211-237. Chem. Abs., 66, 5475.

Park, C.F. and MacDiarmid, R.A., 1970: Ore Deposits. 2nd ed. Freeman and Co., San Francisco. p.350.

Park, J., 1906: Thermal activity in its relation to the genesis of certain metalliferous veins. Trans. New Zld. Inst., 38, 20-39.

Parks, G.A., 1971: Trace Elements in Water: Origin, Fate and Control: Mercury. Exploratory and planning proposal submitted to the National Science Foundation, Stanford University, California.

Parks, G.A., 1973: Trace Elements in Water: Origin, Fate and Control: I - Mercury. Report of progress, March 1972 to Feb. 1973.

Perry, J.H., 1963: Chemical Engineers Handbook. 4th Ed. McGraw-Hill, Tokyo.

Pierce, A.P., Botbol, J.M. and Learned, R.E., 1970: Mercury content of rocks, soils and stream sediments. U.S.G.S. Prof. Paper 713, 14-16.

Rabone, S., 1971: Nagwha Springs sulphur and mercury deposits. Report of field work done for the Consolidated Silver Co., New Zealand.

Riemers, R.S., Burrows, W.D. and Krenkel, P.A., 1973: Total mercury analysis: review and critique. Water Polln. Control Fed., 45 (5), 815-823.

Robinson, B.W., 1973: Sulphur isotope equilibrium during sulphur hydrolysis at high temperatures. Earth Planet. Sci. Letters, 18, 443-550, cf. data in Wilson (1966) and Robinson (1977).

Robinson, B.W., 1977: Oxygen and sulphur isotope composition of sulphate. In Lyon (1977) p.19.

Roedder, E., 1962: Ancient fluids in crystals. Sci. Am., 207 (4), 38-47.

Roedder, E., 1972: Composition of fluid inclusions. U.S.G.S. Prof. Paper 440-JJ.

Roedder, E., 1975: Annotated bibliography of reports dealing with fluid inclusions by E. Roedder.

Ross, C.P., 1942: Some aspects on the geology of quicksilver deposits in the United States. Econ. Geol., 37, 437-465.

Saukov, A.A., 1946: Geochemistry of mercury. Akad. Nauk S.S.S.R., Trudy Inst. Geol. Nauk, 78, 1-129.

Saupe, F., 1973: La Geologie du Gisement de Mercure d'Almaden. Science de la Terre, Mme. 29, C.N.R.S. Nancy, France. (Ph.D. thesis.)

Saupe, F., 1976: oral communication.

Schwarzenbach, G. and Widmer, M., 1963: Die Loslichkeit von Metall-sulfiden, I. Schwarzes Quecksilbersulfid. Helv. Chim. Acta, 46, 2613-2628.

Schmitt, H.H., 1962: Equilibrium Diagrams for Minerals. Geological Club of Harvard, Cambridge, Mass.

Sergeev, Y.A., 1961: Methods of mercurometric investigations. Internat. Geol. Rev., 3 (2), 93-99.

Shcherbakov, V.P., Dvornikov, A.G. and Zakrenichnaya, G.L., 1970: New data on the forms in which mercury occurs in coals of the Donets Basin. Akad. Nauk Ukrayin R.S.R. Dopovidi Ser. B., 32 (2), 126-130. In Fleischer, 1970.

Siegel, S.M., Siegel, B.Z., Eshleman, A.M. and Bachmann, K., 1973: Geothermal sources in distribution of mercury in Hawaii. Environ. Biol. and Med., 81-99.

Skinner, D.N.B., 1966: Ngawha geothermal area, Northland. New Zld. Geol. Surv. Rept. 16, 3-19 and 35.

Skinner, D.N.B., 1976: oral communication.

Skinner, B.J., White, D.E., Rose, H.J. and May, R.E., 1967: Sulphides associated with the Salton Sea geothermal brine. Econ. Geol., 62, 316-330.

Spencer, J.N. and Voight, A.F., 1968: Thermal dynamics of the solution of mercury metal. I. Tracer determinations of the solubility in various liquids. J. Phys. Chem., 72 (2), 464-474.

Stainton, M.P., 1971: Syringe procedure for transfer of nanogram quantities of mercury vapour for flameless atomic absorption spectrophotometry. Anal. Chem., 43 (4), 625-627.

Stewart, M.K., 1975: oral communication.

Stipp, J.J. and Thompson, B.N., 1971: K/Ar ages from the volcanics of Northland, New Zealand. New Zld. J. Geol. and Geophys., 14 (2), 403-413.

Stock, A. and Cucuel, F., 1934a: The distribution of mercury. Naturwissenschaften, 22, 290-333.

Stock, A. and Cucuel, F., 1934b: The determination of the mercury content of air. Deut. Chem. Ges. Ber., 67B, 122-127.

Thompson, B.N., 1965: Broad distribution of volcanic rocks in North Island, New Zealand. In Thompson and Kermode, 1965, p.5-11.

Thompson, B.N. and Kermode, L.O., 1965: Volcanology, New Zealand. New Zld. D.S.I.R., Inf. Series 49, 33-46.

Thompson, G.A., 1954: In Krauskopf, 1951, p.498; ibid, 175-197.

Trost, P.B., 1970: Effects of humic acid type organics on secondary dispersion of mercury. Ph.D. thesis, Colorado School of Mines. In Krenkel, 1974.

Tunell, G., 1964: Chemical processes in the formation of mercury ores and ores of mercury and antimony. Geochim. et Cosmochim. Acta, 28, 1019-1037.

Vinogradov, A.P., 1959: The Geochemistry of Rare and Dispersed Chemical Elements in Soils. 2nd ed. Consultants Bureau Inc., New York.

Vostal, J., 1972: Mercury in the Environment. Friberg and Vostal, eds. Cleveland C.R.C. Press, 215p.

Wagman, D.D., Evans, W.H., Parker, V.B., Halow, I., Bailey, S.M. and Schum, R.H., 1974: Selected values of chemical thermodynamic properties. Nat. Bur. Standards, Table 35 of Series I, Washington.

Waring, G.A., 1965: Thermal springs of the United States and other countries of the world - a summary. U.S.G.S. Prof. Paper 492, 383p.

Weast, R.C., 1976: Handbook of Chemistry and Physics. 56th ed. C.R.C. Press, Cleveland.

Wedepohl, K.H., 1970: Mercury. In Handbook of Geochemistry, ch.80. Springer-Verlag, Berlin, Heidelberg.

Weiss, H.V., Koide, M. and Goldberg, E.D., 1971: Mercury in a Greenland ice sheet: evidence of recent input by man. Science, 174, 692.

Weissberg, B.G., 1969: Gold-silver ore-grade precipitates from New Zealand thermal waters. Econ. Geol., 64, 95-108.

Weissberg, B.G., 1971: Determination of mercury in soils by flameless atomic absorption spectrometry. Econ. Geol., 66, 1042-1047.

Weissberg, B.G. and Wodzicki, A., 1970: Geochemistry of hydrothermal alteration and origins of sulphide mineralization at the Tui mine, Te Aroha, New Zealand. New Zld. J. Sci., 13 (1), 36-60.

Wellman, H.W., 1956: Structural outline of New Zealand. D.S.I.R. Bull., 121, 36p.

Wellman, H.W., 1975: New Zealand 60 m.y. ago. Bull. Aust. Soc. Explor. Geophys., 6 (2-3), 55-56.

Wershaw, R.L., 1970: Sources and behaviour of mercury in surface-waters. U.S.G.S. Prof. Paper 713, 29-31.

Westoo, G., 1967: Determination of methylmercury compounds in foodstuffs II. Acta Chem. Scand., 21 (7), 1790-1800.

Westoo, G., 1968: Determination of methymercury salts in various kinds of biological material. Acta Chem. Scand., 22 (7), 2277-2280.

White, D.E., 1967: Mercury and base-metal deposits with associated thermal and mineral waters. In Geochemistry of Hydrothermal Ore Deposits. H.L. Barnes, ed. Holt, Rinehart and Winston Inc., New York. pp.575-631.

White, D.E., 1968: Hydrology, activity and heat flow of the Steamboat Springs thermal system, Washoe County, Nevada. U.S.G.S. Prof. Paper 458-C.

White, 1976: oral communication.

White, D.E. and Robertson, C.E., 1962: Sulphur Bank, California - a major hot spring quicksilver deposit. Geol. Soc. Am., Buddington Volume, 397-428.

White, D.E. and Waring, G.A., 1963: Volcanic emanations. U.S.G.S. Prof. Paper 440-K.

White, D.E., Barnes, I. and O'Neil, J.R., 1973: Thermal and mineral waters of nonmeteoric origin, California Coast Ranges. Geol. Soc. Am. Bull., 84, 547-560.

White, D.E., Hem, J.D. and Waring, G.A., 1963: Chemical composition of subsurface water. U.S.G.S. Prof. Paper 440-F.

White, D.E., Hinkle, M.E. and Barnes, I., 1970: Mercury content of natural thermal and mineral fluids. U.S.G.S. Prof. Paper 713, 25-28.

White, D.E., Muffler, L.J.P. and Truesdell, A.H., 1971: Vapour-dominated systems compared with hot-water systems. Econ. Geol., 66, 75-97.

Wikander, L., 1968: Mercury in ground and river water. Grundforbaettring, 21, 51-155.

Wilkinson, M.C., 1972: The surface properties of mercury. Chem. Revs., 72 (6), 575-625.

Williston, S.H., 1968: Mercury in the atmosphere. J. Geophys. Res., 73, 7051-7055.

Wilson, S.H., 1966: Sulphur isotope ratios in relation to volcanological and geothermal problems. Bull. Volcanologique, 29, 671-690.

Wood, J.M., 1971: Environmental pollution in mercury. In Advances in Environmental Science Technology. Pitts and Metcalf, eds. J. Wiley and Sons Inc. p.39-56.

Wood, J.M., Penley, M.W. and De Simone, R.E., 1972: Mechanisms for Methylation of Mercury in the Environment. Tech. Repts. Series No.137. Mercury Contamination in Man and His Environment. International Energy Agency, Vienna. p.49-65.

Yates, R.G. and Thompson, G.A., 1959: Geology of the quicksilver deposits of the Terlingua District, Texas. U.S.G.S. Prof. Paper 312.

Young, D.R., Johnson, J.N., Soutar, A. and Isaacs, J.D., 1973: Mercury concentrations in dated varved sediments collected off southern California. Nature, 244, 273-274.

Zautashvili, B.Z., 1966: The problems of mercury hydrogeochemistry, as illustrated by the mercury deposits of Abkhazia. Geokhimiya, 357-362.

Zussman, J., 1969: Physical Methods in Determinative Mineralogy. Academic Press. (re p.215-260 by J.V.P. Long.)

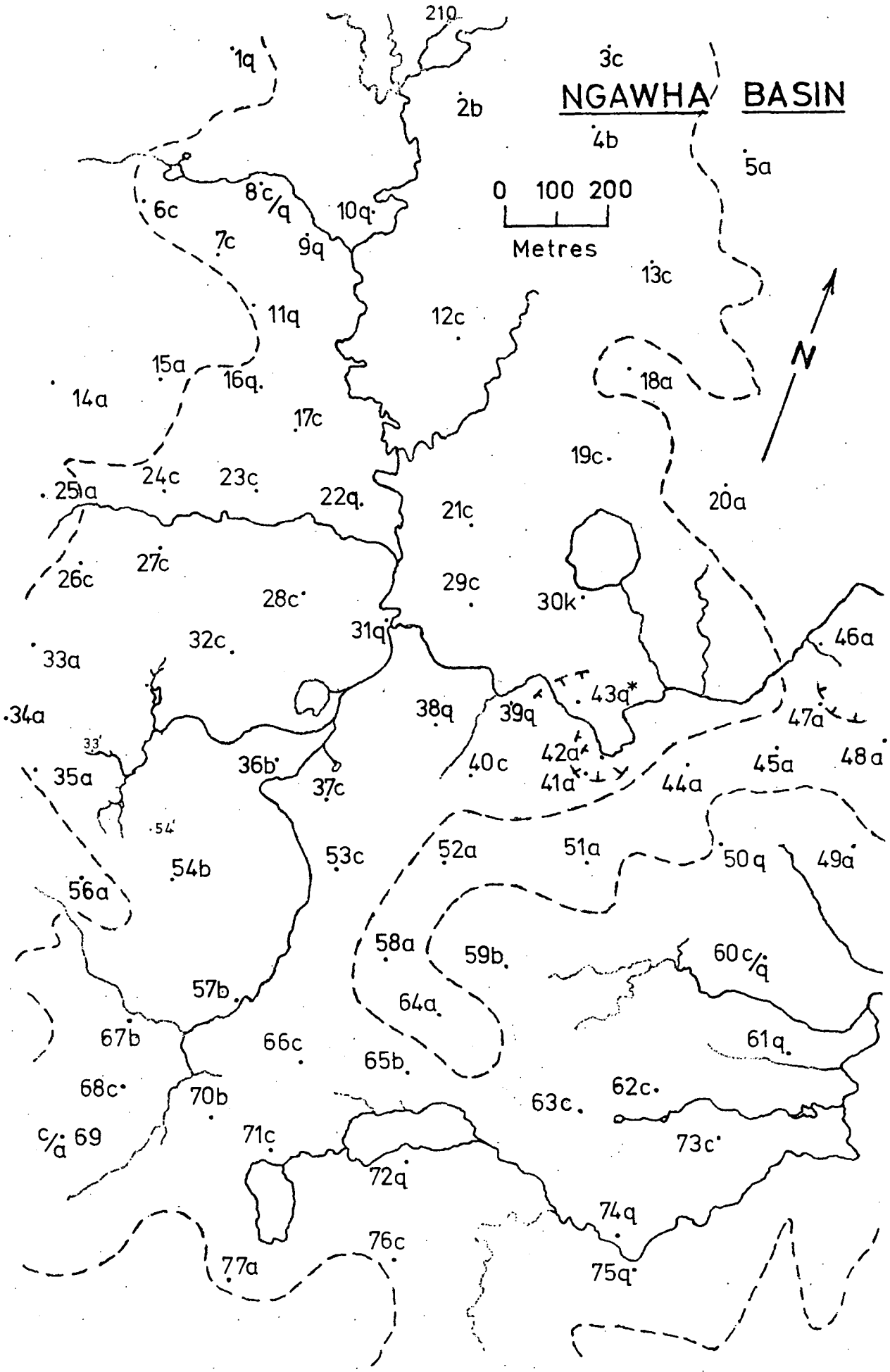


Figure (A.1) Soil Profile Sites

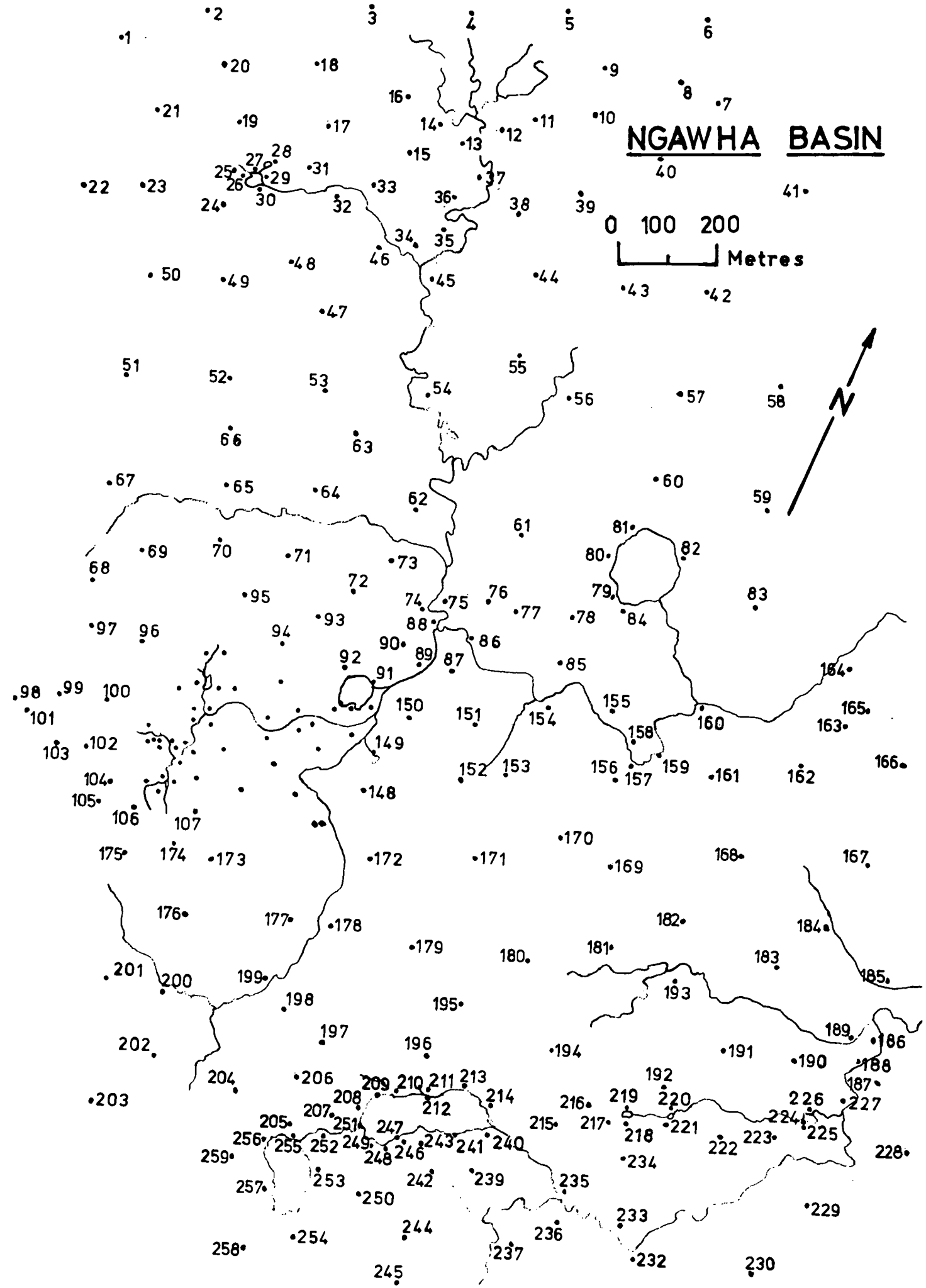


Figure (A.2) Top-Soil Sample Sites

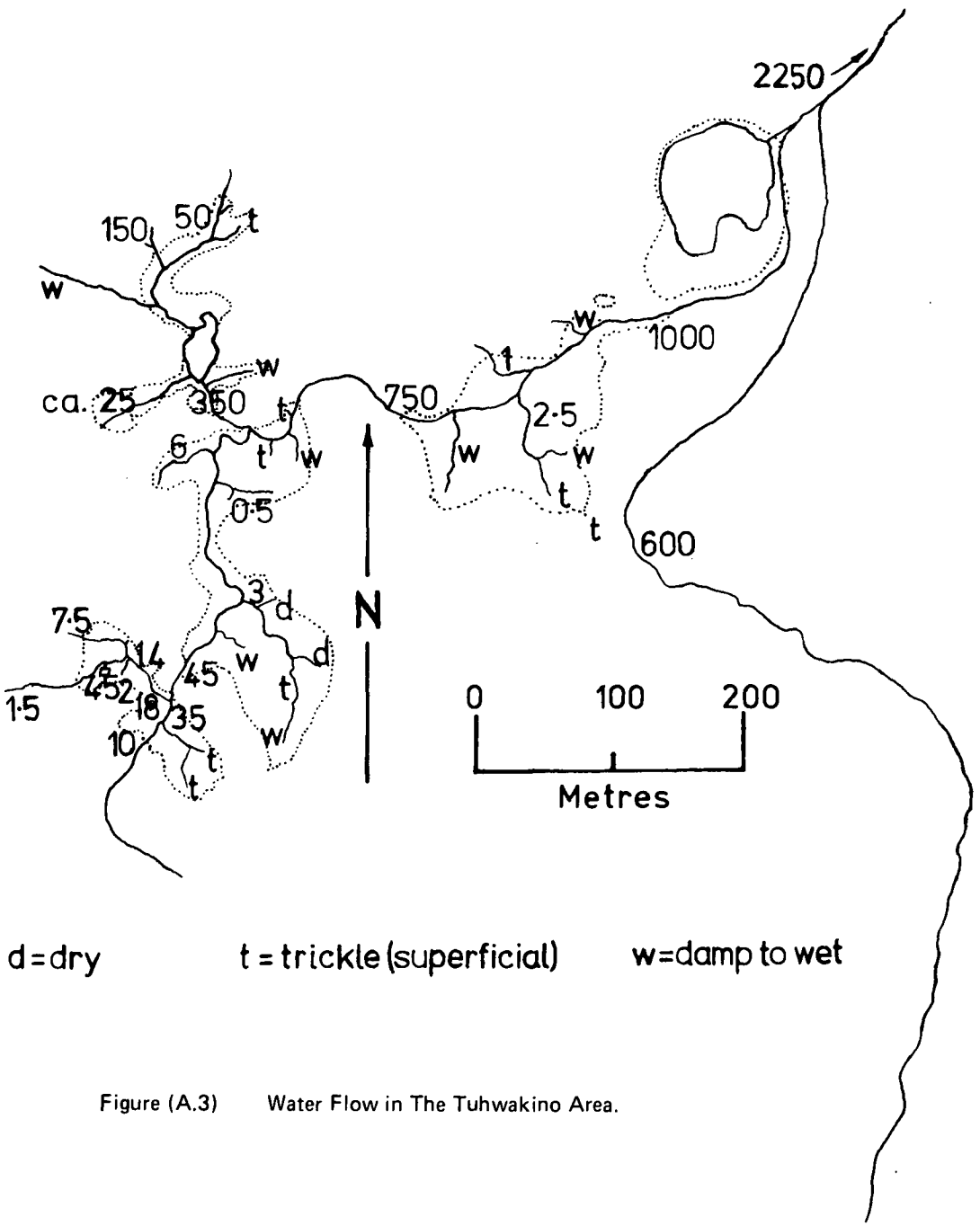


Figure (A.3) Water Flow in The Tuhwakino Area.

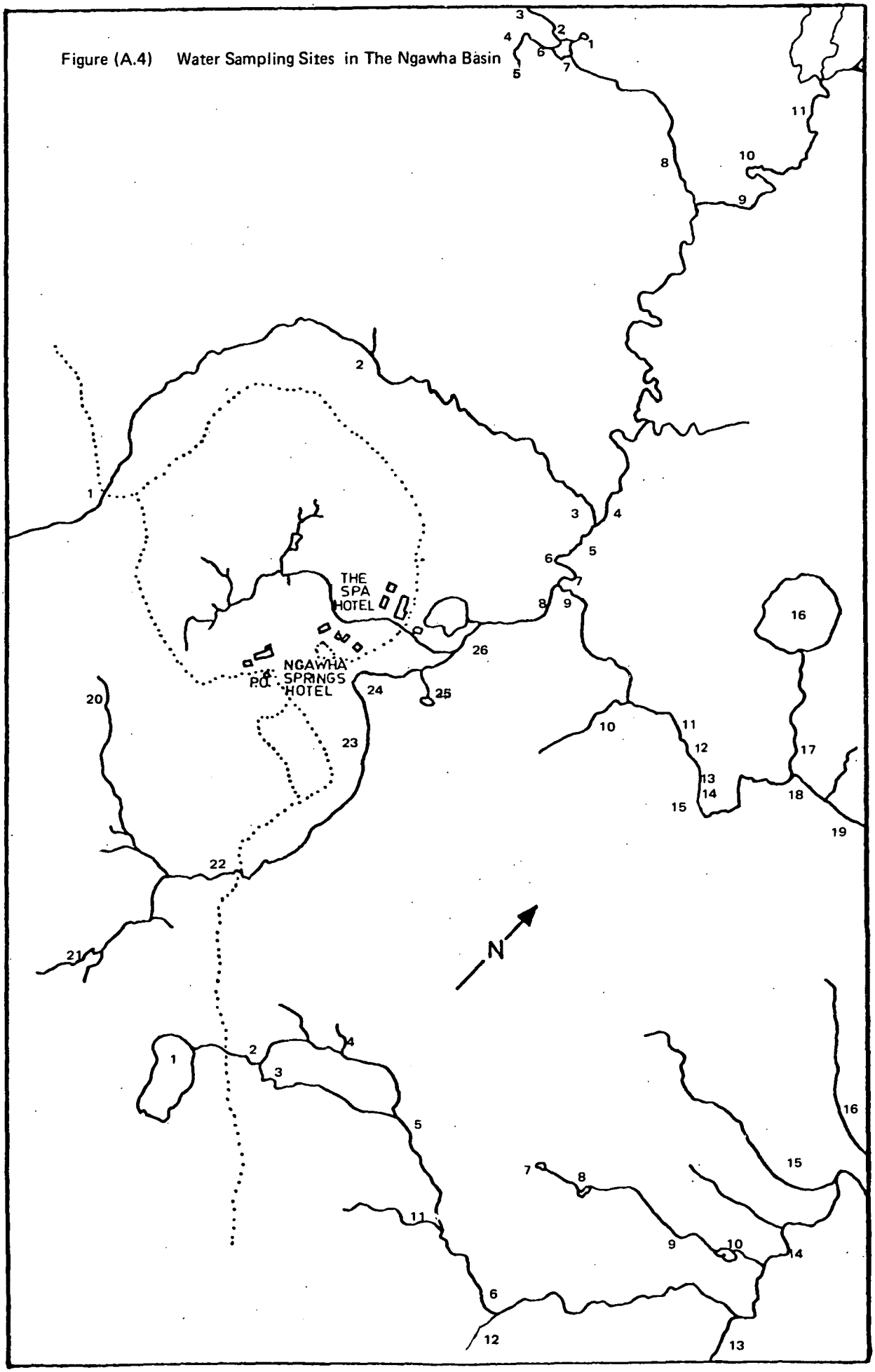


Figure (A.4) Water Sampling Sites in The Ngawha Basin

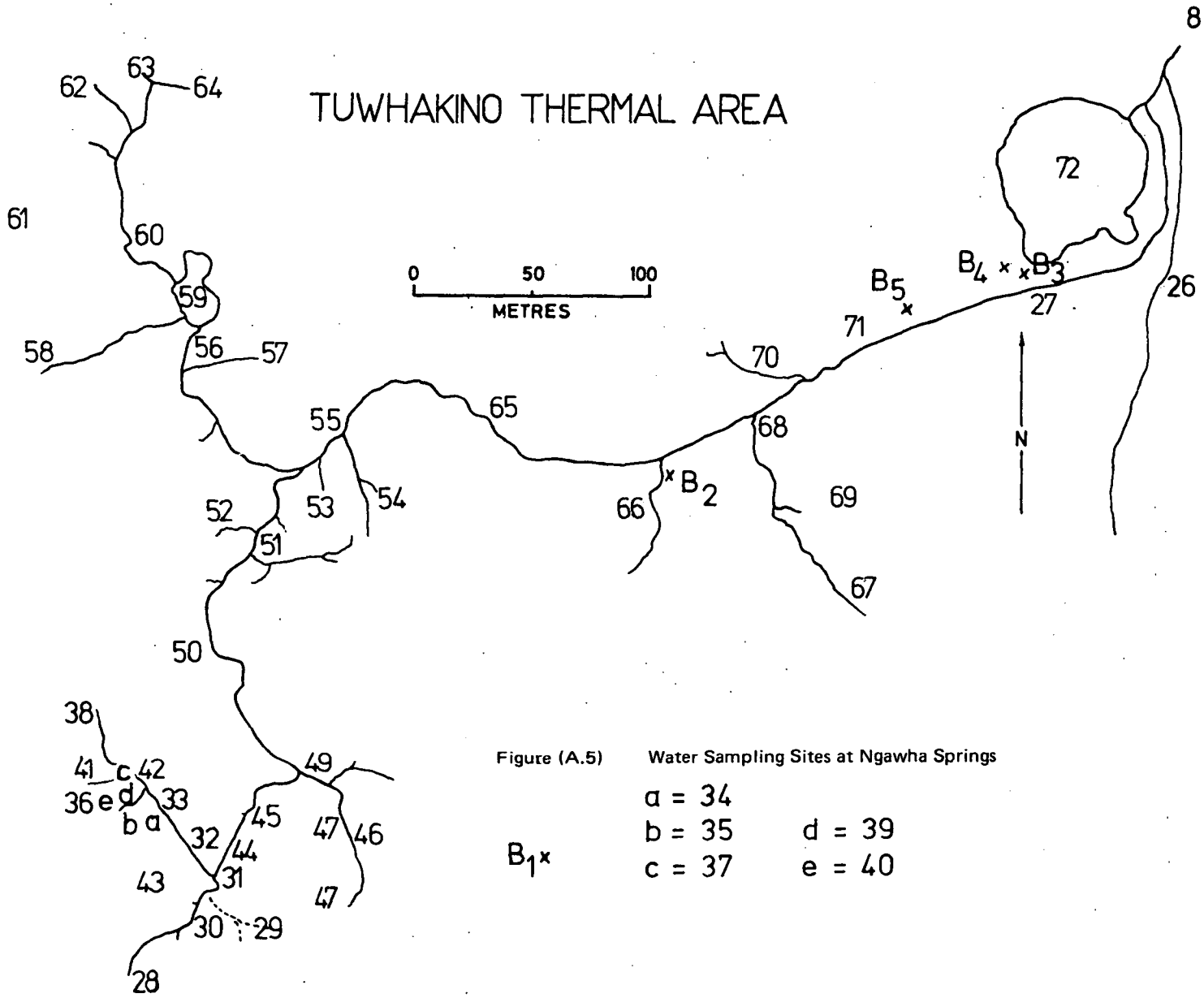


Figure (A.5) Water Sampling Sites at Ngawha Springs

a = 34
b = 35
c = 37
d = 39
e = 40

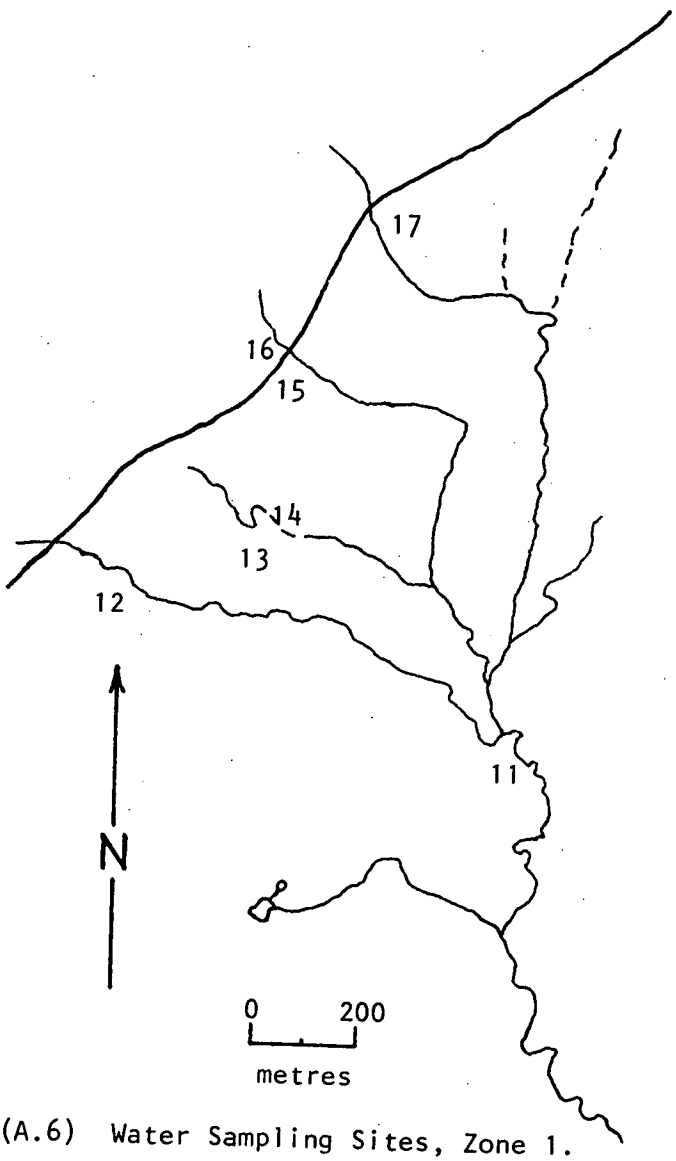


Figure (A.6) Water Sampling Sites, Zone 1.

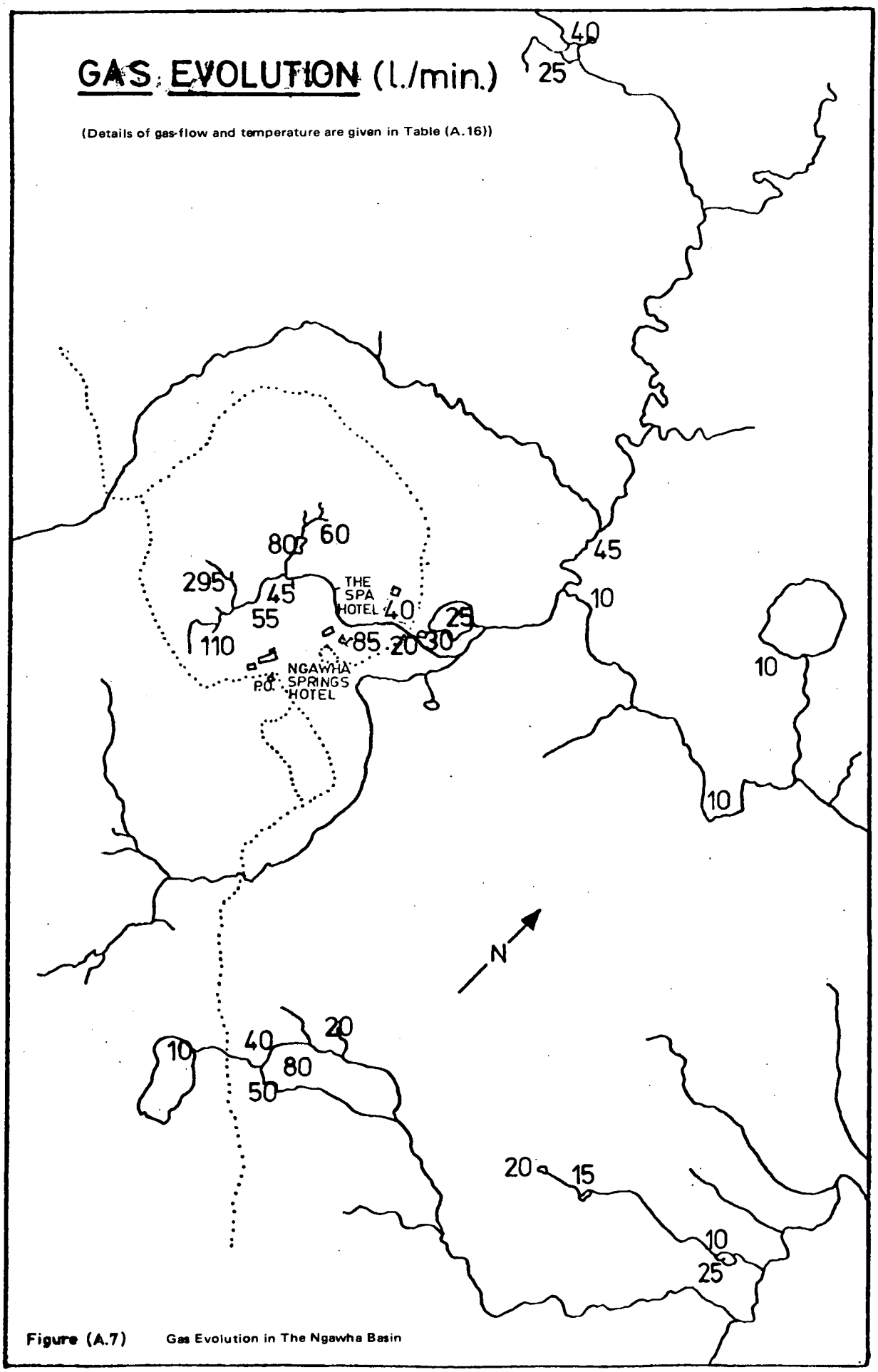


Figure (A.7) Gas Evolution in The Ngawha Basin

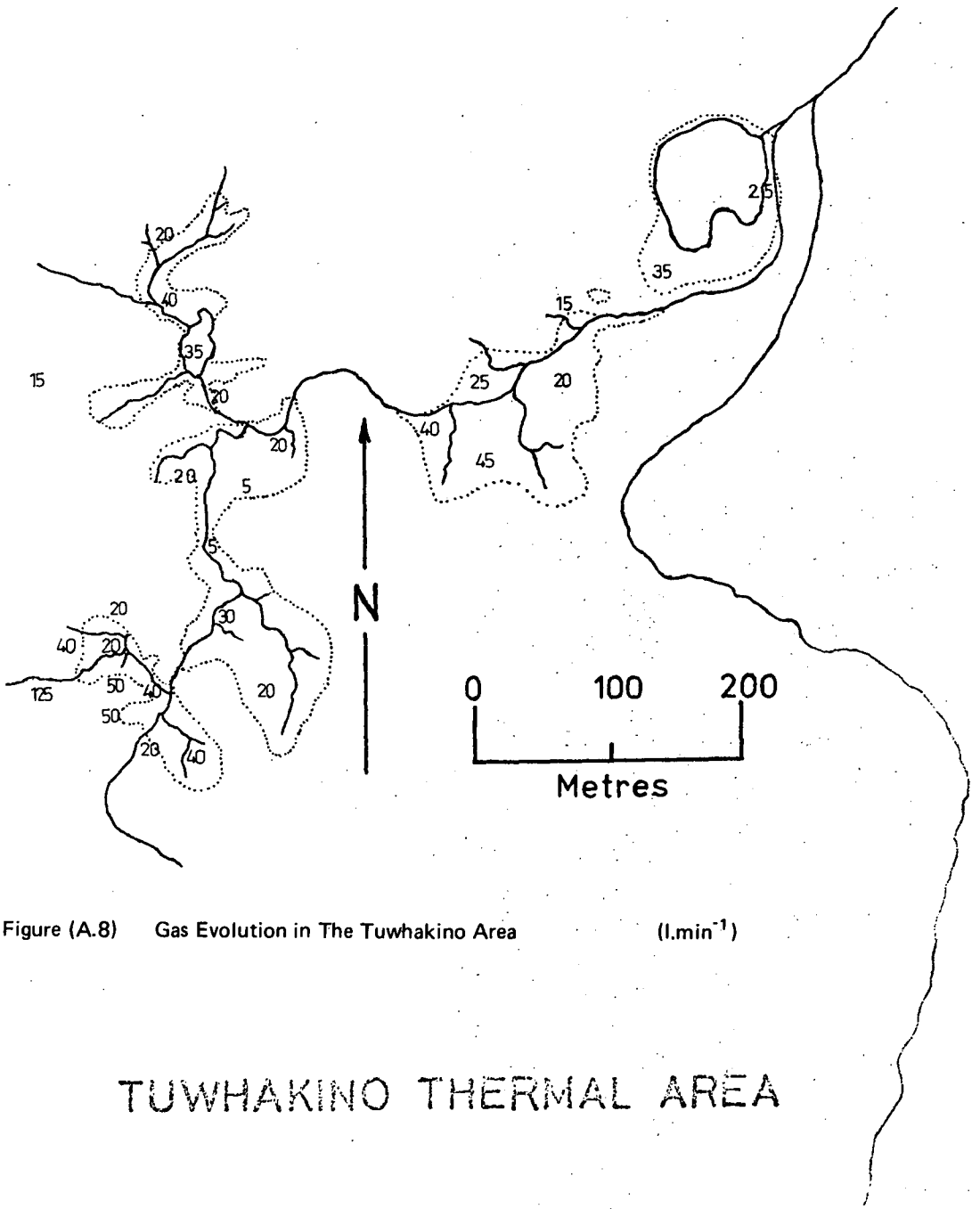


Figure (A.8) Gas Evolution in The Tuwhakino Area ($l.min^{-1}$)

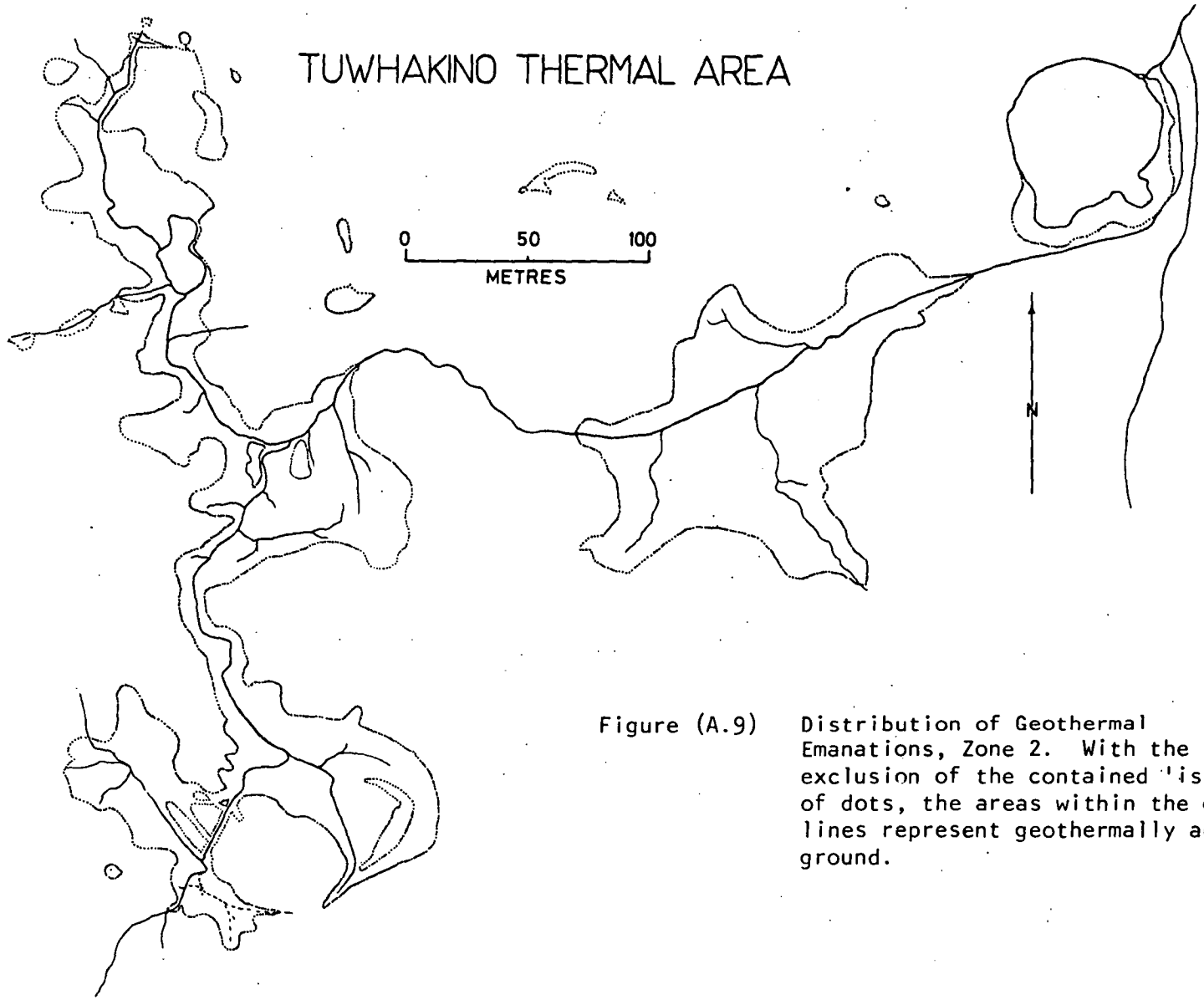


Figure (A.9) Distribution of Geothermal Emanations, Zone 2. With the exclusion of the contained 'islands' of dots, the areas within the dotted lines represent geothermally active ground.

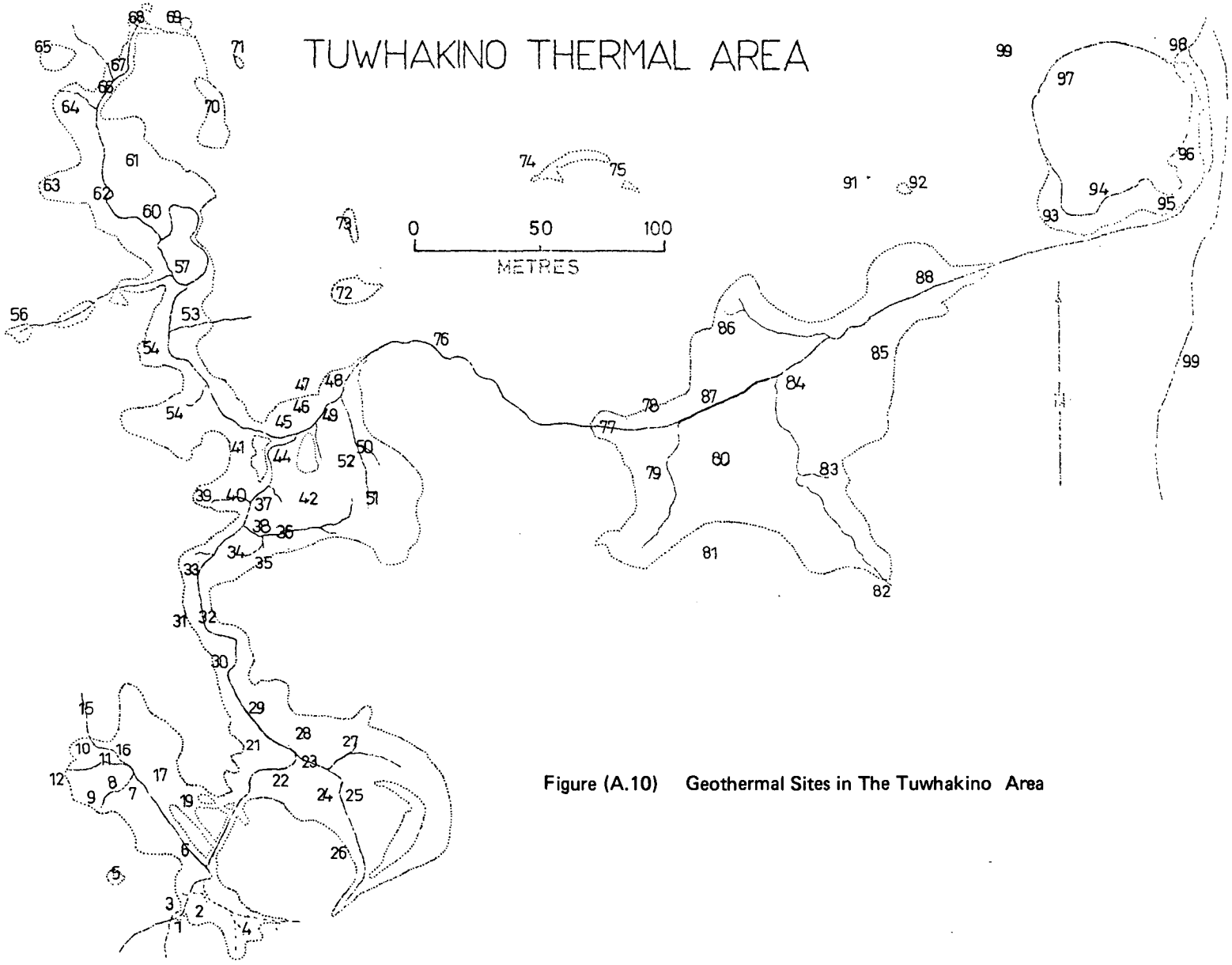


Figure (A.10) Geothermal Sites in The Tuwhakino Area

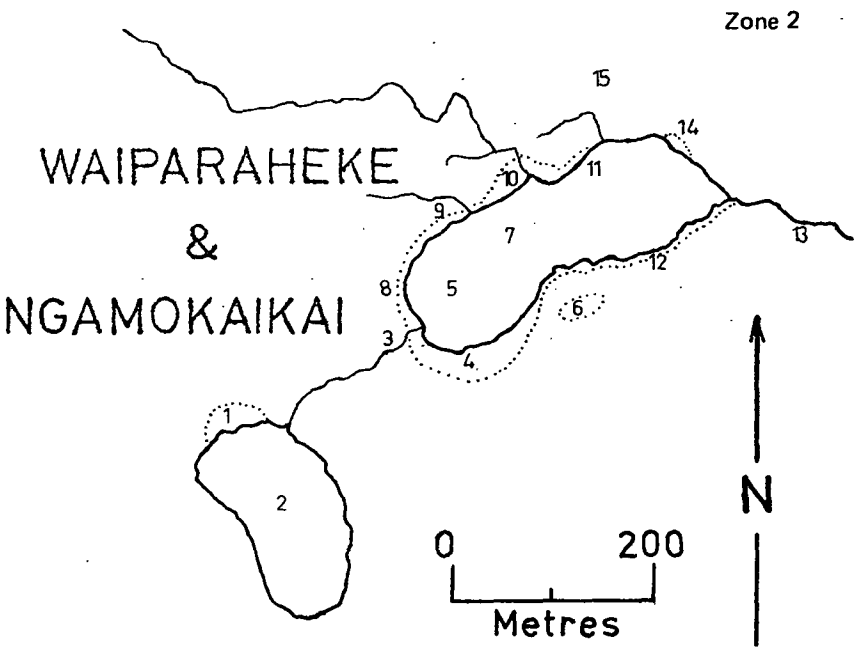
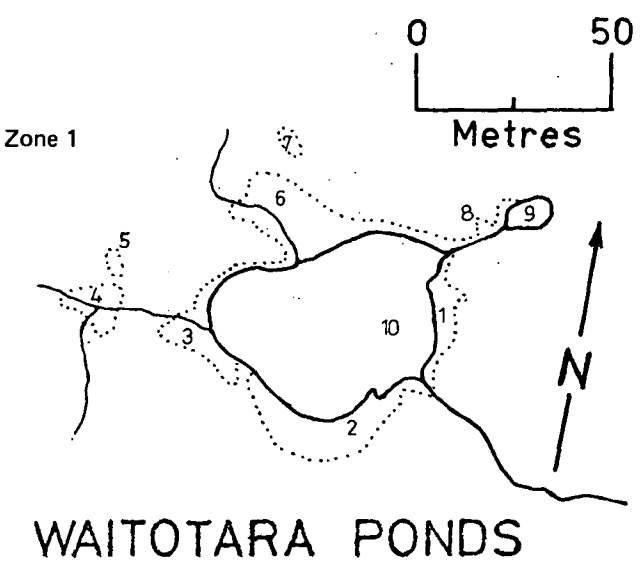


Figure (A.11):
Geothermal Sites of Zones 1 and 2



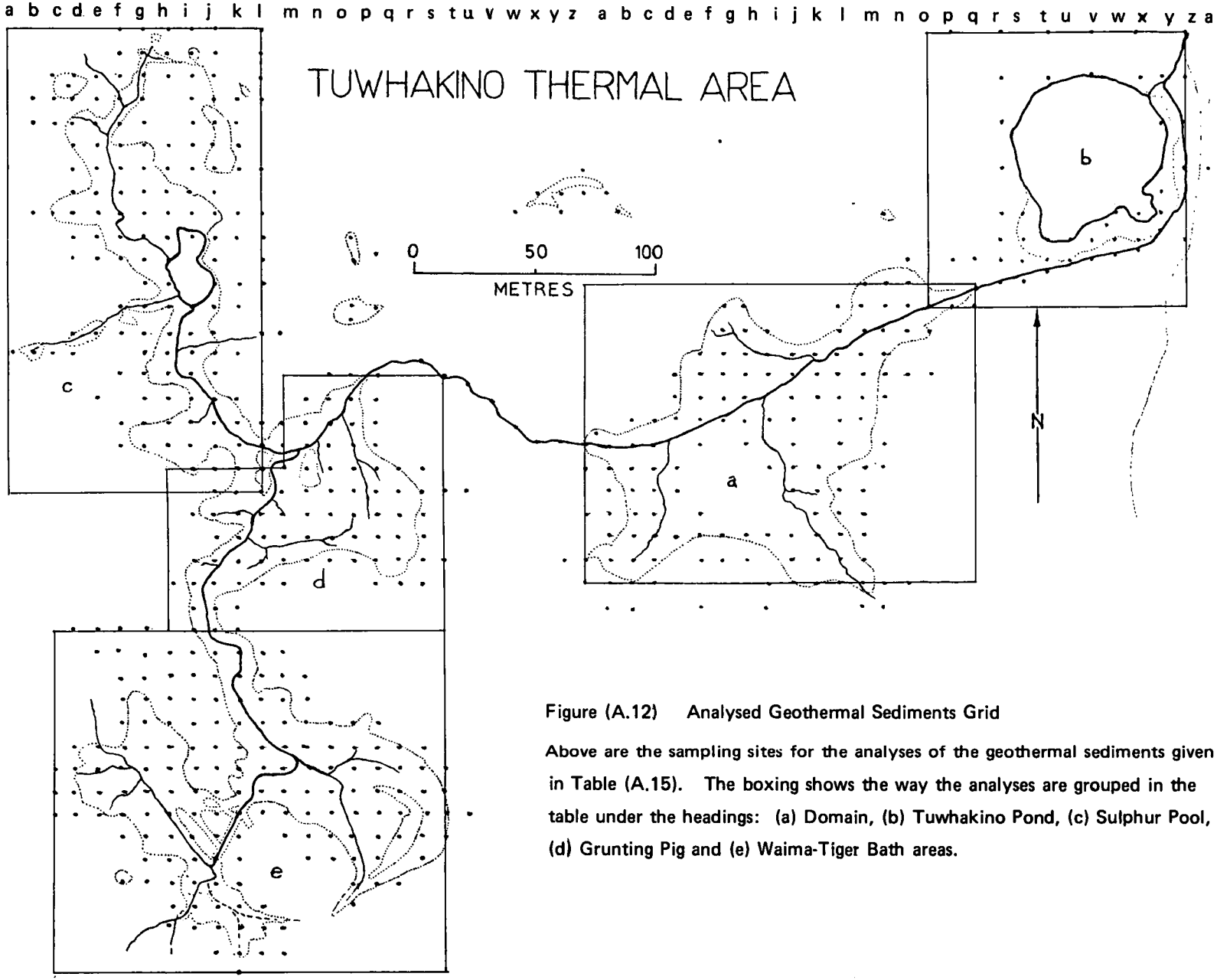


Figure (A.12) Analysed Geothermal Sediments Grid

Above are the sampling sites for the analyses of the geothermal sediments given in Table (A.15). The boxing shows the way the analyses are grouped in the table under the headings: (a) Domain, (b) Tuwhakino Pond, (c) Sulphur Pool, (d) Grunting Pig and (e) Waima-Tiger Bath areas.

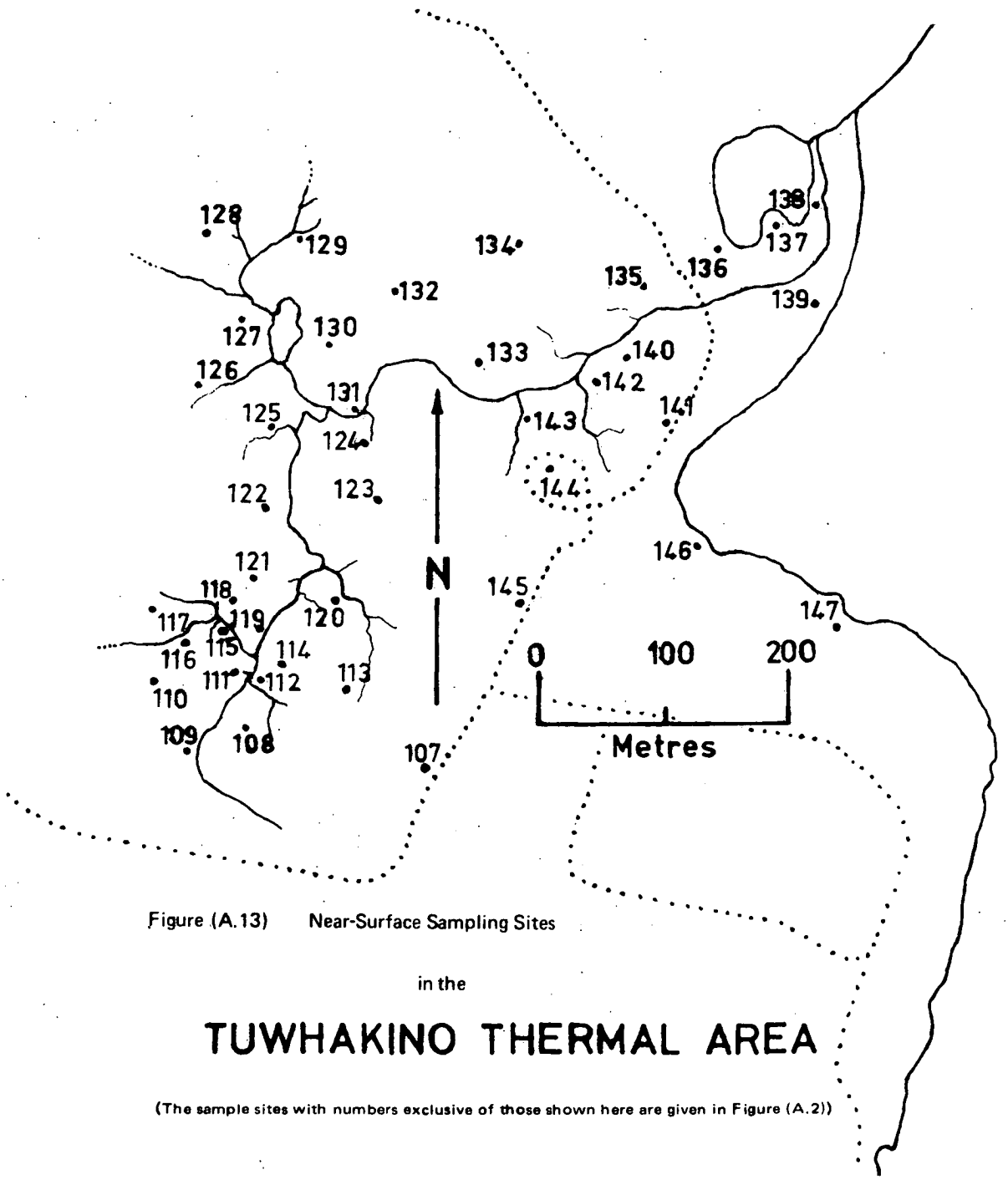


Figure (A.13) Near-Surface Sampling Sites

in the

TUWHAKINO THERMAL AREA

(The sample sites with numbers exclusive of those shown here are given in Figure (A.2))

C

B

A

Figure (A.19) A: Profile M, Lake Sediments with near maximal soil development. The first signs of bedding are at about 35 to 40 cm depth, 1/10x. B: Efflorescences of oxidizing iron in the lake sediments near unexposed basalt in the Tuwhakino area, 1/8. C: An unusually large amount of kaolinite above a chaos breccia profile. Note the thin top-soil. Below the exposed kaolinite is the weathered bedrock. 1/24.

TABLE (A.1) Total Mercury in Soil Horizons: (ppm)

Site†	Type*	Lit	Org	Orch	Lch	Dep	Wrk	Rock
1	b	0.18	0.24	0.20	0.18	0.19	0.12	0.10
2	h/b	0.32	0.40	0.40	0.34	0.26	0.20	0.16
3	s	0.26	0.36	0.40	0.32	0.20	0.16	0.02
4	h/s	0.30	0.38	0.34	0.30	0.22	0.095	0.06
5	c	0.10	0.13	0.12	0.07	0.10	0.08	0.025
6	s	3.4	1.8	1.9	0.90	0.85	0.95	1.2
7	s	0.80	0.50	0.52	0.42	0.36	0.28	0.24
8	s/b	0.64	0.56	0.48	0.40	0.42	0.32	0.22
9	b	0.48	0.46	0.36	0.32	0.36	0.28	0.19
10	b	0.38	0.40	0.34	0.30	0.34	0.32	0.22
11	b	0.32	0.48	0.42	0.32	0.30	0.28	0.16
12	s	0.30	0.32	0.34	0.32	0.18	0.11	0.03
13	s	0.12	0.24	0.20	0.28	0.17	0.08	0.015
14	c	0.30	0.34	0.30	0.26	0.07	0.12	0.32
15	c	0.40	0.34	0.34	0.28	0.08	0.17	0.30
16	b	0.26	0.38	0.36	0.28	0.24	0.22	0.18
17	s	0.28	0.36	0.30	0.34	0.26	0.12	0.08
18	c	0.22	0.36	0.38	0.32	0.06	0.09	0.28
19	s	0.12	0.46	0.40	0.36	0.07	0.09	0.075
20	c	0.32	0.30	0.26	0.20	0.07	0.08	0.015
21	s	0.54	0.48	0.46	0.40	0.36	0.38	0.40
22	b	0.38	0.40	0.40	0.38	0.34	0.24	0.14
23	s	0.52	0.48	0.38	0.12	0.08	0.08	0.13
24	s	0.48	0.44	0.36	0.18	0.08	0.11	0.20
25	c	0.42	0.40	0.28	0.14	0.08	0.17	0.28
26	s	0.48	0.48	0.36	0.16	0.11	0.26	0.36
27	s	0.52	0.46	0.34	0.14	0.09	0.18	0.34
28	s/?b	0.38	0.38	0.32	0.28	0.32	0.28	0.11
29	s	0.52	0.60	0.46	0.36	0.16	0.24	0.58
30	t	9.0	16	19	30	46	38	52
31	b	0.42	0.40	0.36	0.36	0.32	0.30	0.14
32	s	1.7	1.4	2.2	3.0	5.6	6.4	9.2
33	c	0.64	0.74	0.66	0.54	0.32	0.34	0.38
34	c	0.015	0.025	0.02	0.07	0.11	0.12	0.32
35	c	0.52	0.56	0.50	0.19	0.17	0.28	0.44
36	t	3.8	4.0	4.8	5.4	4.6	3.8	2.0

TABLE (A.1) Cont.

Site†	Type*	Lit	Org	Orch	Lch	Dep	Wrk	Rock
37	s	0.60	1.1	0.52	0.40	0.18	0.15	0.04
38	b	0.36	0.44	0.38	0.32	0.24	0.20	0.07
39	b	0.48	0.56	0.36	0.36	0.32	0.30	0.06
40	s/?c	0.68	0.58	0.40	0.36	0.22	0.24	0.28
41	c	0.18	0.22	0.20	0.16	0.12	0.30	0.65 a 0.02 0.33
42	c		0.44	0.44	0.32	0.34	0.42	b 0.014 0.54
43	b	0.22	....	1.5 dry		0.28	0.04	0.075
44	c	0.32	0.34	0.32	0.24	0.10	0.11	0.30
45	c	0.42	0.32	0.30	0.26	0.08	0.22	0.34
46	c	0.32	0.40	0.36	0.28	0.09	0.26	0.64
47	c	0.24	0.42	0.30	0.32	0.20	0.28	0.42
48	c	0.36	0.34	0.32	0.28	0.13	0.30	0.34
49	c	0.18	0.28	0.24	0.18	0.20	0.26	0.22
50	b	0.32	0.34	0.28	0.24	0.22	0.14	
51	c	0.26	0.38	0.32	0.18	0.08	0.12	0.28
52	c	0.36	0.32	0.30	0.26	0.11	0.17	0.30
53	s	0.42	0.40	0.38	0.32	0.16	0.20	0.19
54	h	0.62	0.68	0.68	0.36	0.32	0.24	0.13
55	c		0					
56	c	0.03	0.05	0.08	0.07	0.07	0.09	0.34
57	h	0.20	0.38	0.36	0.30	0.08	0.12	0.18
58	c	0.30	0.30	0.26	0.22	0.08	0.19	0.28
59	h	0.28	0.38	0.26	0.20	0.17	0.18	0.22
60	s/b	0.22	0.32	0.30	0.26	0.30	0.24	0.20
61	b	0.26	0.26	0.18	0.20	0.19	0.024	0.03
62	s	0.30	0.34	0.46	0.50	0.48	0.54	0.56
63	s	0.28	0.32	0.34	0.32	0.46	0.60	0.54
64	c	0.26	0.24	0.19	0.11	0.08	0.11	0.13
65	h	0.26	0.28	0.32	0.44	0.20	0.22	0.28
66	s	0.17	0.14	0.12	0.08	0.05	0.06	0.06
67	h	0.24	0.32	0.28	0.19	0.12	0.07	0.06
68	s	0.20	0.22	0.19	0.13	0.09	0.07	0.05
69	s/c	0.18	0.22	0.18	0.14	0.06	0.05	c 0.025 0.14
70	s	0.22	0.22	0.21	0.16	0.07	0.09	0.20

TABLE (A.1) Cont.

Site†	Type*	Lit	Org	Orch	Lch	Dep	Wrk	Rock
71	s	0.16	0.18	0.24	0.18	0.12	0.10	0.13
72	?b	0.80	0.88	0.82	0.76	0.52	0.34	0.16
73	s	0.28	0.30	0.22	0.085	0.06	0.02	0.02
74	b	0.22	0.24	0.20	0.19	0.16	0.11	0.06
75	b	0.18	0.22	0.20	0.16	0.17	0.12	0.055
76	s	0.18	0.20	0.19	0.15	0.07	0.04	0.04
77	c	0.14	0.16	0.13	0.07	0.06	0.03	0.015

a: The analyses are for i the calcareous shale; ii the limestone boulders and iii the average chaos breccia. b: analyses for the i limestone and ii the chaos breccia. * See Table (A.2) footnote. † Located in Figure (A . 1).

TABLE (A.2) Elemental Mercury in Soils (ppm)

		DEPTH INTERVAL (cm)								
Site†	Type*	0-10	10-20	20-30	30-40	40-50	50-60	60-70	70-80	80-95
1	b	0.006	0.005	0.022	0.030	0.032	0.036	0.030	0.030	0.028
6	s	0.015	0.018	0.031	0.034	0.052	0.068	0.091	0.19	0.16
30	t	0.012	0.016	0.038	0.046	0.050	0.052	0.048	0.058	0.72
32	s	0.002	0.003	0.003	0.008	0.01	0.013	0.024	0.034	0.058
33'	s/c	0.013	0.015	0.020	0.024	0.028	0.037	0.040	0.038	0.044
54'	h/s	0.019	0.032	0.052	0.058	0.066	0.078	0.082	0.086	0.094
62	s	0.005	0.014	0.006	0.031	0.038	0.034	0.036	0.033	0.038
65	h	0.004	0.009	0.012	0.016	0.027	0.031	0.034	0.028	0.026
71	s	0.008	0.010	0.011	0.014	0.015	0.018	0.021	0.025	

† Sites are located in Figure (A . 1)

* Soil Type Key refers to the contributing bedrock compositions and the profile development.

b	=	basalt
c	=	chaos breccia
h	=	peat
s	=	lake sediments
t	=	geothermal sediments
h/b	=	peat soil over basalt
s/b	=	lake sediments over basalt
s/c	=	lake sediments over chaos breccia
h/s	=	peat soil over lake sediments.

TABLE (A.3) Elemental Mercury in The Top-Soil* (ppm)

Site†	Concentration	Site	Concentration	Site	Concentration
1	0.003	35	0.006	75	0.007
2	0.005	39	0.007	76	0.022
3	0.0056	40	0.006	77	0.014
4	0.002	41	0.002	78	0.021
5	0.006	42	0.0025	79	0.035
6	0.005	43	0.002	80	0.018
7	0.003	44	0.003	81	0.013
8	0.006	45	0.002	82	0.016
9	0.02	46	0.003	83	0.007
10	0.013	47	0.004	84	0.028
11	0.008	48	0.012	85	0.009
12	0.011	49	0.01	86	0.007
13	0.0045	50	0.007	87	0.003
14	0.008	51	0.002	88	0.0045
15	0.012	52	0.003	89	0.004
16	0.011	53	0.002	90	0.004
17	0.006	54	0.002	91	0.34
18	0.004	55	0.002	92	0.023
19	0.024	56	0.006	93	0.008
20	0.014	57	0.002	94	0.021
21	0.012	58	0.002	95	0.0085
22	0.002	59	0.002	96	0.016
23	0.010	60	0.008	97	0.015
24	0.024	61	0.011	98	0.002
25	0.028	62	0.005	99	0.01
26	5.2	63	0.007	100	0.016
27	4.4	64	0.024	101	0.003
28	0.13	65	0.021	102	0.018
29	15.	66	0.007	103	0.006
30	0.38	67	0.006	104	0.023
31	0.011	68	0.019	105	0.020
32	0.05	69	0.012	106	0.027
33	0.0015	70	0.017	107	0.022
34	0.002	71	0.013	108	0.46
35	0.004	72	0.006	109	0.039
36	0.009	73	0.007	110	0.16
37	0.002	74	0.005	111	0.43

TABLE (A.3) Cont.

Site†	Concentration	Site	Concentration	Site	Concentration
112	1500.	149	0.009	186	0.005
113	0.13	150	0.004	187	0.002
114	0.27	151	0.003	188	0.003
115	4200.	152	0.006	189	0.008
116	380.	153	0.008	190	0.005
117	170.	154	0.003	191	0.007
118	26.	155	0.006	192	0.02
119	.3	156	0.013	193	0.012
120	5700	157	0.012	194	0.012
121	110	158	0.010	195	0.007
122	60	159	0.012	196	0.011
123	220.	160	0.011	197	0.004
123	9.	161	0.003	198	0.006
125	280	162	0.002	199	0.005
126	490	163	0.007	200	0.003
127	240	164	0.005	201	0.002
128	58	165	0.006	202	0.002
129	15	165	0.006	203	0.002
130	60	167	0.001	204	0.006
131	440	168	0.0015	205	0.011
132	210	169	0.004	206	0.007
133	86	170	0.008	207	0.008
134	33	171	0.009	208	0.017
135	360	172	0.012	209	0.025
135	900	173	0.006	210	0.022
137	500	174	0.017	211	0.036
138	470	175	0.017	212	0.048
139	280	176	0.003	213	0.022
140	47	177	0.007	214	0.020
141	160	178	0.014	215	0.011
142	2750	179	0.008	216	0.020
143	720	180	0.011	217	0.022
144	52	181	0.011	218	0.037
145	85	182	0.0045	219	0.039
146	0.012	183	0.007	220	0.026
147	0.004	184	0.002	221	0.021
148	0.004	185	0.003	222	0.026

TABLE (A.3) Cont.

Site†	Concentration	Site	Concentration	Site	Concentration
223	0.017	219	0.022	255	0.016
224	5.1	240	0.026	256	0.01
225	0.048	241	0.032	257	0.005
226	0.033	242	0.012	258	0.002
227	0.01	243	0.040	259	0.006
228	0.003	244	0.002		
229	0.004	245	0.003		
230	0.004	246	0.044		
231	0.006	247	1.1		
232	0.004	248	19.		
233	0.004	249	80.		
234	0.015	250	0.003		
235	0.003	251	56.†		
236	0.003	252	0.007	268	0.019
237	0.004	253	0.014	269	0.028
238	0.014	254	0.003		

† See Figure (A.2)

* The top-soil is the uppermost ca. 35 cm.

TABLE (A.4) Analysis of Iron Mineral Occurrences (%, *)
(* denotes parts per million)

		Fe	S	Si	A1	K	Ca	Hg	Fe/S#
1	Hm, p	69.6	2.6					5*	26.8
2	Hm/Py, w	2.87	7.26	57.47				22.26 Cu, 10.1	12.1
3	?Hm, s	1.86	1.58	38.97			39.39	7.25	4.70
4	Hm, s/n	19.04	8.58	56.89				0.95 Mn, 14.29	2.22
5	Hm, p	2.23	1.03	48.8				ca 0.03	2.16
6	Ms/Hm, n	12.58	7.33	40.76	31.97	low	7.33	0.04	1.72
7	?FeS, pn	62	37					0.12	1.676
8	Hm/Ms, p	59.77 Na, 0.11;	37.18	2.77 Cu, 37*;	0.13 Sb, 45*;	0.07 Se,	0.09 5*;	0.19 Zn, 16* &	1.61 Pb, <6*
9	s	9.2	5.8	39.9	24.8	0.61	12.9	Zn, 9*	1.586
10	s	0.715	4.16	31.88	28.46	11.01	2.38	20.08	1.16
11	s	0.63	8.60	35.20	5.87		low	49.16 Cu, 0.55	1.047
12	Ms/Py, s	46.28	51.50					ca 0.1 Sb, 2.18	0.899
13	Ms, p	46.78	53.21					0.15 Sb, 0.06	0.879
14	Py, f	46.08	52.90	n.d.					0.871
15	Ms, n	40.49	47.80	11.67				1.28	0.84
16	Ms, n	42.44	56.33	1.22					0.753
17	Ms, n	37.47	49.77	12.75					0.75
18	Ms, n	39.16	57.52	3.32				100*	0.68
19	Ms, n	29.67	51.06	19.27					0.58
20	pMs, s	12.1	67.8	2.9				10.3	0.17
21	S, s	3.07	19.86 Cu, 27*;	41.44 Sb, 2.09	1.57	0.99 Se, 35*;	0.19 Zn,	3.1 16* & Pb,	0.16 16*

a Key to the mineral occurrences:

p = pipelet, f = scum on hot pool, w = on wood, s = (in) stream sediments, pn = actively forming pipelet, n = nodule, pMs = oxidising marcasite pseudomorph, Ms = marcasite, Hm = haematite, Py = pyrite, ?FeS = sulphide of approximate composition FeS and S = Sulphur.

The ratio of iron to sulphur is based on the sulphur remaining after subtraction of the stoichiometric requirements for other sulphides present. (% Fe/% S for marcasite and pyrite is 0.87).

Note that for samples 12 and 21 that the Sb concentration is in per cent.

TABLE (A.5) Country Rock Analyses for Majors and Traces (%, *)

* denotes parts per million

Reference	1	2	3	4	5	6	7	8	9
SiO_2	26.65		90.26	47.00	78.11	48.39	86.97	23.09	73.71
Al_2O_3	3.51		4.80	17.27	1.73	17.31	0.90	3.65	8.91
Fe_2O_3†	58.88	<0.5	0.48	9.31	1.23	9.32	0.22	1.54	5.69
MgO	0.36		0.49	5.13	0.25	4.85	0.15	0.88	2.14
CaO	0.17		0.61	11.39	0.16	10.85	0.15	38.31	3.15
Na_2O	0.12		0.12	3.45	0.20	3.49	0.26	0.66	1.67
K_2O	0.00		0.55	0.91	0.69	1.00	0.13	0.61	2.28
H_2O^+	11.57	96.43	2.27	3.39	11.99	2.39	11.19	29.20	1.57
TiO_2	0.20		0.17	1.77	0.23	1.82	0.09	0.21	0.94
P_2O_5	0.10		0.00	0.30	0.00	0.32	0.00	0.11	0.16
MnO	0.10		0.00	0.16	0.13	0.19	0.00	0.10	0.09
Hg	0.25*	3.5*	0.016*	0.26*	17.*	0.066*	23.*	0.003*	0.016*
As	< 6*	<3*	<3*	<3*	5*	<3*	4*	<3*	
Cu	23*	⩽2*	<2*	57*	27*	51*	4*	40*	
Pb	<6*	<6*	<6*	11*	16*	<6*	< 6*	9*	
Sb	<7*	6*	6*	< 5*	2.1	109*	48*	<5*	
Zn	122*	⩽2*	4*	140*	16*	64*	8*	44*	
Se	<3*	3*	<2*	<2*	35*	<2*	<2*	<2*	
Total	101.67	96.43	99.75	100.10	96.93	99.98	100.07	100.17	

1 = weathered basalt from N15/353348

2 = coal from Kawakawa

3 = chaos breccia (the least weathered) from N15/358345

4 = basalt (drill-core from below Ngawha Springs Hotel)

5 = geothermal sediments (Tuwhakino area)

6 = basalt from N15/378349

7 = sinter from Waitotera Pond

8 = limestone mass in chaos breccia

9 = lake sediments from N15/383334

† all Fe has been analysed as Fe_2O_3

TABLE (A.6) Mercury in Miscellaneous Materials (ppm)

Rust flakes	228
Leptosperum species (Tea-tree)	256
Human hair, (from head) before visit	1.1
Human hair (from head, after 3½ months	1.2
Human hair (from head), resident of 4 years	3.8
Tankwater 'Spa' Hotel	0.0015
Tar, local fumarole condensate at Waima	68
Tar, Tiger area	150
Tar, thin layer in sediments at Waima	120
Tar, formed from buried Kauri vegetation at J*	94
Wood from base of Tiger Bath	33500
Wood, charred at mound A*	24000
Wood, hydrothermally altered from B*	78000
Wood, waterlogged, not very altered	12000
Copper wire, ca. 0.7 mm diameter	2500
Pyrite cubes ca 1 mm diameter	300
Pyrite/marcasite tubelets	800
Marcasite/pyrite tubelets with cinnabar film	10000
Marcasite tubelets	1500
Pseudomorphed wood, fresh	1000
Pseudomorphed wood, some weathering	5000
Organic mercury in fresh condensate, Waima	0.00035
Limonite from N15/376350	0.002

* refers to profile site area, see Table (A.23).

TABLE (A.7) Mercury in Sediments* (ppm)

Streams	Reference	km from Basin	Range			Mean
Tiger area	15/364355	0.0	600	to	1050	900
Waima		0.0	500	to	800	700
Adj. flat		0.0	400	to	3.1%	450
Sulphur Pool		0.0				350
Domain		0.0	200	to	650	450
Adj. A		0.0	350	to	800	500
'Spa' bridge		0.0	300	to	350	300
Tuwhakino	15/372352	0.0	40	to	75	60
Ngawha	15/372352	0.0	8	to	50	40
Waterfall, below	15/376351	0.35	16	to	30	20
Small slip	15/378350	0.8	5	to	35	15
Big slip, upstream	15/383358	1.5	5	to	10	6.5
Big slip	15/384358	1.6	3	to	6.5	5
Waiaruhe River	15/434417	10	2.5	to	8	5
Waiaruhe River	15/473468	21	0.7	to	6	1.5
Waitangi River	15/517489	33	0.1	to	0.25	0.20
Waitangi River	11/554507	40	0.1	to	0.6	0.22
Waitangi Estuary	11/559506	41	0.2	to	0.5	0.3

Pools	Temperature	Gas Flow	Range			Mean
Waitotera	cool 18 – 24	low to high	10	to	900	200
Tuwhakino	cool 19 – 23	moderate	36	to	600	200
Milky Way	hot ca 40	low to mod.	1000	to	1250	1200
Jubilee	hot ca 55	low	500	to	800	600
Tiger	hot ca 40	v. high	1000	to	25000	10000
Lowest Sulphur P.	cold ca 19	low to mod.	2	to	45	30
Waiapawa	cold 19	low to zero	1	to	30	6
Waiparaheke	cold 18 – 22	low to high	4	to	150	25
Ngamokaikai	cold 18	zero to low	0.15	to	28	ca 2

* The minus 85 - mesh fraction of the sediments was analysed.

TABLE (A.8) Cinnabar Analyses (%)

Sample	Hg	S	Si	Fe	A1	Cu	K	Other
1	85.1	14.9						
2	42.9	7.51	49.5					
3	49.2	8.62	35.2	0.628	5.87	0.551		
4	20.1	4.20	31.8	0.715	28.5		11.02	Ca 2.38
5	84.2	15.8						
6	42.9	12.4	26.0	15.6		2.57		
7	85.6	14.4						
8	44.8	16.8	38.1			1.051		
9	87.7	12.4						
10	18.34	11.24	57.5	2.87		10.08		
11	28.0	33.1	31.7		6.93			
12	50.7	8.25	32.5		7.12			
13	7.25	1.58	39.0	1.86	9.28	0.05	1.65	Ca 39.4
14	2.54	0.414	70.9		24.6	1.167		
15	21.7	4.53	29.9	1.08	10.4		1.37	Ca 31.1
16	46.9	7.92	34.1	0.17	11.0			
17	42.8	13.3	32.2	0.14	11.5			
18	41.6	13.2	34.0	0.17	11.0			
19	44.2	11.9	39.8		4.16			
20	46.7	12.5	36.4		4.274			
21	33.1	6.09	17.5	0.204		0.204		Zn 0.098 Sb 0.116 Ca 32.6
22	47.1	13.7	27.9	0.51	10.1	0.72		
23	82.2	13.1	3.22			1.14		
24	28.1	31.5	29.6		6.34			
25	3.4	0.85	0.41		0.3		0.15	C mostly

(Pure stoichiometric cinnabar contains 86.2% mercury).

TABLE (A.9) Average Total Mercury in Country Rocks (ppm)

Rock Type	Location	Mercury
Chaos Breccia	slip, 15/378350	0.33
Chaos Breccia (15/383358)	Mangamutu Stream	0.26
Chaos Breccia (shale)	Mangamutu Stream	0.65
Chaos Breccia	Ngawha Stream	0.36
Chaos Breccia (15/358345)	above road	0.015
Limestone in Chaos Breccia	slip 15/378350	0.022
Calcite veining in Chaos	in boulders at slip	0.070
Limestone	Opahi	0.056
Limestone	Pokapu	0.0028
Lake Sediments	15/375334	0.0056
Lake Sediments	15/375363	0.0080
Kaolinite, white	15/357345	0.072
Kaolinite, white	15/363343	0.070
Kaolinite, white	15/384354	0.08
Andesite, Wairakau	Taipa	0.009
Rhyolite	Putahi (dome)	0.02
Basalt	15/376351	0.015
Basalt (ca. 45° C)	15/367343	0.25
Basalt	15/377351	0.066
Basalt	15/381344	0.015
Basalt	15/368344	0.26
Basalt	15/336393	0.014
Basalt	15/377380	0.025
brecciated basaltic andesite	15/383348	0.25
Montmorillonite	Domain	1.45
Montmorillonite	N15/366360	0.30
Montmorillonite	N15/381344	0.25
Montmorillonite	N15/397347	0.24
Limonite (in bog)	N15/376352	0.0015
Limonite	Waiparaheke Pond	0.14
Kawakawa Coal	N15/571378	4.3
Sinter	Waitotera Pond, N.E.	0.23
Sinter	Waitotera P., E.N.E.	2.4
Sinter	as above	20000.
Basement Sediments (siltstone)	ca. 2.5 km W. Moerewa	0.035
Sandstone (?Mata Series)	ca. N15/356338	0.002 - 0.03

TABLE (A.10) Mercury Species in Soil Horizons (ppm)

HORIZON	DEPTH (cm)	SPECIES OF MERCURY		
PROFILE A(t)	Organic	Elemental	Cold Extr.	Total
1	0 - 18	0.030	2.7	0.008	21000
2	- 20.5	0.004	2.0		8000
3	23.5	0.0025	3.9	0.0495	19000
4	27.5	0.002	7.8	0.010	6500
5	32.5	0.001	10.6		6000
6	40.5	0.0016	31		5200
7	53	0.002	46	0.009	5100
8	64	0.005	59		5600
9	67.5	0.004	56		6800
10	72.5	0.001	63		5900
11	89	3.6	190	0.1	12000
12	114.5	2.25	780	0.094	9000
13	129	1.6	1600		2800
14	139	0.9	800		850
15	149	0.007	770	0.0096	1100
16	169	0.0014	1450		4700
17	ca. 300	0.00002	2400	0.13	5100
PROFILE B (t)					
humus	0	0.45	1.95	0.1	1100
1	0 - 0.25	0.075	120		2800
2	- 45	10.3	1500		105000
3	48	0.003	7000		140000
4	135.5	0.0004	8400		120000
5	ca. 250				27000
PROFILE C (c)					
humus		0.00015	0.007	0.002	0.12
1	0 - 25	0.00002	0.009	0.003	0.21
2	60	0.00001	0.03	0.006	0.26
3	ca. 200	0.00001	0.04	0.005	0.28
4	ca. 360	n.d.	0.065	0.005	0.33
PROFILE D (t)					
humus		0.00093	0.07	0.0021	6.2
1	0 - 0.5	0.0002	0.19	0.0026	25
2	3.0	0.00013	15.5/0.25	0.0039	29
3	4.25	0.00004	0.36	0.0041	22

TABLE (A.10) Contd.

PROFILE D(t) (Contd).		Organic	Elemental	Cold Extr.	Total
4	13.25	0.00002	0.46	0.0055	36
5	28.5	0.000012	0.53	0.0046	41
6	41.3		0.97	0.0048	68
7	56		7.6	0.0057	81
8	61		9.2	0.0049	84
9	84		9.5	0.0036	76
10	95	0.000001	10.6	0.0042	64
11	118		10.7	0.0048	85
12	132		10.9	0.0067	89
13	158		12.2	0.0064	96
14	187		13.6	0.0078	88
15	225.5		15.6	0.0062	93
16	261.5		18.3	0.0083	97
17	290.5		32	0.0096	102
18	308		38	0.011	130
19	336		51	0.011	160
20	370.5	0.00008	67	0.013	230
21	398.5		106	0.017	590
22	422.5		112	0.024	670
23	456		119	0.053	720
24	484		320	0.069	940
25	ca. 520	15.	340	0.078	1100
PROFILE E (t)					
humus		0.0009	0.06	0.006	1.9
1	0 - 6	0.0003	0.19	0.005	2.3
2	13	0.00006	0.22	0.008	5.4
3	31	0.00002	0.59	0.009	6.8
4	36	0.0008	0.95	0.009	7.3
5	65	0.0003	7.1	0.016	18.
6	97	0.012	18	0.019	97
7	160	0.000035	44	0.032	121
8	165	n.d.	50	0.007	465
9	239	n.d.	58.5	0.038	450

TABLE (A.10) Contd.

PROFILE F (h)		Organic	Elemental	Cold Extr.	Total
humus		0.00014	0.03	0.0014	2.6
1	0 - 2.5	0.0003	0.51	0.0021	2.9
2	4.5	0.0001	0.68		5.8
3	12	0.00005	0.73		5.3
4	17	0.00002	0.93		6.4
5	21.5		0.95	0.0057	4.9
6	26.5		0.97		5.4
7	28.5		1.68		6.8
8	38		2.8		7.2
9	40.5		5.9		7.5
10	55.5	n.d.	6.3	0.041	7.4
11	83		5.8		6.7
12	93.5		6.9		8.1
PROFILE G (h)					
humus		0.00019	0.055	0.0014	3.1
1	0 - 0.23	0.0005	35	0.0042	54
2	38	0.0002	46	0.0060	40
3	67	0.00008	52	0.0084	61
4	97	0.000035	63	0.0058	80
5	115	n.d.	78	0.0097	92
6	126	n.d.	91	0.0105	96
PROFILE H (s)					
humus		0.0008	0.035		0.7
1	0 - 4.5	0.0003	0.02	0.002	0.5
2	7.5	0.0004	0.03		0.4
3	13	0.0002	0.05		0.56
4	34	0.00009	0.06		0.9
5	39	0.00005	0.08		1.2
6	41.5	0.00002	0.15		1.4
7	49	0.00004	0.37		2.5
8	52.5	0.00005	2.1		3.4
9	79	0.00002	4.7		13.5
10	120	0.00001	5.2		82
11	190	n.d.	7.6		144

TABLE (A.10) Contd.

PROFILE I (c)		Organic	Elemental	Cold Extr.	Total
humus	0	0.0002	0.002	0.0005	0.02
1	2.8	0.00012	0.003		0.024
2	78	0.000025	0.005		0.06
3	88	n.d.	0.02		0.075
4	320	n.d.	0.06		0.32
PROFILE J (t)					
humus	0	0.00035	0.027	0.0032	0.6
1	0.3	0.00008	0.038	0.0038	1.6
2	0.9	0.00003	0.052	0.0047	3.5
3	6.0	0.00002	0.057	0.0076	11.
4	7.5		0.064	0.0062	8.8
5	12.5		0.073	0.0088	9.8
6	50.5		0.088	0.0104	13.8
7	80		0.096	0.020	17.1
8	111		0.106	0.027	18.9
9	141		0.11	0.041	25.6
10	202		0.12	0.052	31.5
11	267	0.0000035	0.138	0.073	41
12	287		0.156	0.085	105
*13	110 - 145	0.023	0.11	0.0094	110

* 5 m upstream from J

PROFILE K (c)					
humus	0	0.0004	0.0016		0.006
1	4.5	0.00017	0.0024		0.028
2	17.5	0.00002	0.0058		0.08
3	350	n.d.	0.0079		0.092
4	375	n.d.	0.0074		0.5
PROFILE L (t)					
humus	0	0.002	2.8	0.01	1800
1	12.5	0.0003	180	0.025	6600
2	27.5	0.006	270	0.11	150000
3	45	0.0004	310		3900
4	80	0.0008	340		2400
5	110	0.0002	860		5800
6	170	0.0009	2700		6900
7	210	0.00002	300 1200		1100
*8	225				

* next lower horizon, not in profile cutting, 1 m to south

TABLE (A.10) Contd.

PROFILE M (t/s)		Organic	Element	Cold Extr.	Total
humus	0	0.00086	0.03	0.0036	0.76
1	3	0.00015	0.050	0.0037	31.
2	4.5	0.00009	0.058	0.0045	13.5
3	6.75	0.000034	0.069	0.0087	32.6
4	8.5	0.000011	0.078	0.0071	18.9
5	36.5	0.000004	0.084	0.0077	11.4
6	39	0.00001	0.097	0.011	60
7	49	n.d.	0.105	0.017	44
8	65		0.117	0.054	73
9	ca.160		0.124	0.066	88
10	ca.290		0.15	0.135	165
PROFILE N (s)					
humus	0	0.0003	n.d.	0.0017	0.045
1	9	0.0007	0.004	0.0019	0.05
2	50	0.00001	0.0075	0.0014	0.09
3	75	n.d.	0.011	0.0006	0.11
4	230	n.d.	0.010	0.0008	0.11
PROFILE O_a (t)					
humus †	0	0.003	0.023	0.018	4
1	3	0.0035	0.055	0.023	38
2	7.5	0.005	0.19	0.036	46
3	22.5	0.018	1.4	0.034	72
PROFILE O_b (t)					
humus	0	0.0006		0.0002	6
1	0.5	0.0001			9
2	60	0.00002	0.26	0.0015	15
3	195		0.48		32
4	235		0.52		45
5	243		0.88		78
6	285	0.53	15	0.45	68

† detrital litter

TABLE (A.10) Contd.

PROFILE O_c (t)		Organic	Element	Cold Extr.	Total
humus	0		0.0018		0.32
1	0.5		n.d.		4
2	135		0.01, 2.1		1.2, 8
3	165		1.3		14
4	167		3.8		31
5	207		1.4, 2.4		26
6	213	0.00001	2.7		46
7	253	0.004	10.5		52
PROFILE P (c)					
humus	0	0.0007	0.02		0.07
1	0.15	0.00004	0.05		0.08
2	300		0.006		0.14, 0.22
3	800		0.009		0.34
4	ca. 1,500		0.05		0.64
PROFILE Q (b)					
humus	0	0.0006	0.0008		0.004
1	0.5	0.0008	0.002		0.006
2	40	0.0002	0.0016		0.023
3	52.5		0.0035		0.062
4	57	n.d.	0.0042		0.07
PROFILE R (h)					
humus	0	0.0015	0.04	0.0034	0.2
1	20	0.0004	0.05	0.0042	0.8
2	25	0.00007	0.008	0.00084	1.1
3	55		0.004	0.0005	0.9
4	175		0.005		0.6
PROFILE S (t)					
1	13	0.2	45	0.0095	350
2	31	2.3	400		1500
3	45	0.7	530		1200

TABLE (A.10) Contd.

PROFILE T (c)		Organic	Element	Cold Extr.	Total
humus	0	0.0004	0.002	0.0003	0.11
1	3.5	0.000011	0.005		0.09
2	18		0.004		0.07
3	80	n.d.	0.0035		0.08
4	185		0.006		0.13
5	365		0.008		0.25
PROFILE U (t)					
1	9	0.003	13	0.017	1700
2	19.5		28		400
3	35		40		520
4	50		36		440
5	60		38		480
6	70		32		420
7	85		36		460
PROFILE V (t)					
humus	0	0.0011	0.65	0.0018	8.6
1	3.8	0.0004	3.2	0.0044	29
2	8	0.0001	10.1	0.019	90
3	11	0.00003	18.6	0.013	130
4	43	0.00002	96	0.064	550
5	58	0.00001	128	0.057	530
6	90	n.d.	157	0.069	640
7	121	n.d.	195	0.079	750
8	170		220	0.090	830
9	220	n.d.	280	0.116	890
10	270				850

TABLE (A.11) Mercury in Ngawha Waters (ppm)

Site †	Mercury	Site	Mercury	Site	Mercury
ZONE 1					
1	0.0087	7	0.102	13	.....
2	0.11	8	0.0017	14	0.001
3	0.3	9	0.0012	15	.....
4	0.0036	10	0.0013	16	0.0005
5	.....	11	0.004	17	0.0003
6	0.035	12	0.0005		
ZONE 2					
1	0.0014	28a	0.029	55	3.5
2	0.0019	28b	0.12	56	0.0435
3	0.0017	28c	0.147	57	0.07
4	0.0013	29a		58	high locally
5	0.0014	29b		59	0.042
6	0.0013	30a	0.033	60a	0.019
7	0.012	30b		60b	0.025
8a	0.0045	31	0.083	61	0.018
8b	0.0012	32	0.029	62	
9	0.0014	33		63	0.0084
10	0.0017	34		64	0.01
11	0.0014	35	0.70	65a	0.09
12	0.0013	36	0.0265	65b	0.028
13a	0.0008	37	0.46	65c	0.195
13b	0.00005	38	0.0315	66	
14	0.0017	39	0.66	67	0.0035
15	0.0013	40	0.72	68	0.024
16	0.0155	41a	0.075	69	0.082
17	0.0013	41b	0.35^{+}	70	
18	0.0013	42	0.147	71	0.043
19	0.0016	43	0.06	72	0.055
20	0.0015	44	0.072	73	
21		45	0.059		
22	0.0028	46			
23	0.003	47	0.35		
24	0.0036	48b	0.046		
25	0.0016	49	v high		
26	0.019	50	0.3^{+}		
27	0.014	51	v high		
		52	0.0745		
		53	v high		
		54a	0.018		

TABLE (A.11) Contd.

Site	Mercury	Site	Mercury	Site	Mercury
ZONE 3					
1a	0.039	7	0.0073	14	0.0025
1b	0.0024	8	0.007	15	0.0023
2	0.003	9	0.0049	16	
3	0.0169	10	0.0084	17	0.0019
4	0.0031	11	0.0012	18	0.0010
5	0.013	12		19	
6a	0.0017	13	v low		

† sites are located in Figures (A.4) to (A.6).

TABLE (A.12) Elemental Mercury in Gases (μgm/litre)

Location †	Temp.	Hg^o	Location	Temp.	Hg^o
Tiger Bath	43	96	Upper T Stream §	19	15
Tiger Bath	58	260	Upper T Stream	18	14
Small Tiger Bath	32	34	Lower T Stream	18	14
High Tiger Bath	24	20	Waitetera Pond	31	36
15m S.E. of Tiger	61	270	Waitetera Pond	24	20
Pool 4m N. of Tiger	30	35	Waitetera Pond	20	15
Waima, large pool	20	14	Small Waitetera	18	12½
Waima, small pool	28½	30	Ngamokaikai Pond	19	14
Waima, central	25	24	Waiaparaheke Pond	22	18
Flat	22	18	Waiparaheke Pond	25	26
Flat	27	28	Waiparaheke pond	20	15
Flat	24	20½	Waiparaheke Pond	20	12
Sulphur Pool	25	32	Sulphur Ponds	20	15
Sulphur Pool	24	20	Sulphur Ponds	23	19
Sulphur Pool	23	19	Sulphur Ponds	24	19
Sulphur Pool	19	14	Lower Ngawha Stream	18	n.d.
Domain	19	14	372353 Te Pukoro	18	trace
Domain	30	32	Waiapawa	19	15
Domain	23	20	Cinnabar Bath	28	38
Domain	24	18½	Milky Way Bath	36	65
Spa Hotel, S.W. side	16	11	Lobster Bath	39½	72
Gate/366347, frost	1	2½	Cinnabar Bath	41	80
Tuwhakino Pond	26½	25	Jubilee Bath	52	170
Tuwhakino Pond	21	16	Hole near Tiger	90	785
Tuwhakino Pond	20	16	Adjacent Tiger *	72	595
35 m WSW of S Pool	30	33	Profile D, 1m S.	34	45
Domain	38	64	Grunting Pig	24	22
Domain	47	110	Below Profile A	27	26
Cinderella Bath	40	58			

§ T denotes Tuwhakino. * Adjacent Tiger was a shallow hole ca. 1.5 m deep made into the hottest part of the local terrain; the highest temperature in 1973 was recorded at 90°C. Collection by both an oxidizing acid solution and water dis- were used.

† Locations are given in Figures (A .7), (A . 8) and (3 . 8).
(A number of other gases were semi-quantitatively checked for mercury. The results were recorded (high, low or medium), but they are not presented in this thesis).

TABLE (A.13) Analyses of Stream Sediments in Thermal Areas (%)

	Si	A1	Hg	S	Fe	Ca	K	Other
1	75.10	4.98	0.91	10.06	8.67	0.27		
2	70.87	24.62	2.54	0.414				Cu, 1.16
3	53.62	30.15	trace			16.23		
4	51.91	35.36					12.73	
5	48.80	31.01		1.032	2.231	16.93		
6	40.78	31.96		7.33	12.60	7.334		
7	39.90	24.79		5.803	9.20	12.88	0.613	Ti, 2.23
8	39.80	4.16	44.18	11.96				
9	36.45	4.27	46.73	12.54				
10	35.20	5.87	49.16	8.62	0.628			Cu, 0.55
11	32.24	11.50	42.85	13.28	0.139			
12	31.88	28.46	20.08	12.50	0.715	2.385	11.02	
13	29.91	10.40	21.66	4.525	1.075	31.06	1.37	
14	27.54		33.11	6.09	0.204			Ca, 32.5
15	27.86	10.08	47.09	13.94	0.508			Cu, 0.72
16	27.18	6.76	54.78	11.42				
17	10.72	8.48		44.39	34.24	2.16		
18	3.223		82.16	13.11				Cu, 1.14

TABLE (A.14) Mercury Isotope Ratios*

Material	Site	$^{198}Hg/^{202}Hg$	$^{204}Hg/^{202}Hg$
Soil	Profile V, 18°C	0.3421	0.2316
Pipelets	Tiger, 85°C	0.3300	0.2267
Cinnabar	Tiger, 40°C	0.3713	0.2258
Breccia	N15/378350	0.3616	0.2225
Literature †	---	0.3361	0.2299

* From Low (1974) and personal communications

† Nier (1950).

TABLES (A.15)* Mercury in The Tuwhakino Geothermal Sediments

TABLE $(A.15)_a$ Total Mercury Analyses of The Domain Area

	l	m	n	o	p	q	r	s	t	u	v	w	x	y
c	240	160												
p		140												
o		280	240		90									
n	220	360	320		220									100
m	200	280	360	420	340	249		110	94					96
l	170	260	380	480	620	360	220		120	200	160	120	105	240
k		120	300	360	2300	280	200	220	160	240	260	160	160	110
j				280	900	1400	260	360	280	760	220	180	120	120
i				320	380	160	240	340	260	480	200	120	140	110
h			280	260	460		420		180			130		98
g		160	320	280	2800	380	800	420				160	110	
f		100	260	300	200	280	260					1101	120	
e				110	220	240	320	480			280	105	100	
d					88	120	950	2600	320	260		120		
c							105	280	300	160	140	140	120	
b							94	1050	140	120	120	110	180	120
a								180	100	120	86	92	94	110

* Locations of sampling site are in Figure (A .12)

TABLE $(A.15)_b$ Total Mercury Analyses Around Tuwhakino Pond

	o	p	q	r	s	t	u	v	w	x	y	z	a
a		9.0		5.8		6.0		5.2		5.0		5.8	
b													
c				8.2		12		26		16	6.2	5.6	
d													
e				13							360	15	
f													
g				8.6							280	38	12
h											240		
i				82	120				460	320	160		
j				130	240	380	360	420	220	260	140	86	
k		460	60	86	94	78	110	72	74	66			
l			240	98	84	68							
m	280	140	160	low									

TABLE $(A.15)_d$ Total Mercury of The Grunting Pig Area.

	p	q	r	s	t	u	v	w	x	y	z	a
t						180			220			
s					160	400	160	180	160	240		
r				1400	320	280	280	240	300	180		
q	94	120	100	210	740	1100	260	200	240	160		
p	110	640	580	1600	500	420	220	320	180			
o	86	760	420	350	6400	1500	920	540	200			
n		68	980	1100	180	1200	860	380	240			
m			520	1200	4000	580	460	720	440	200		
l					180	260	280	580	1600	380		
k					220	280	1340	320	95000	720	260	600
j					260	160	1800	260	1400	1200	380	460
i					380		420		1700	2200	560	320
h					240							2200

TABLE $(A.15)_c$ Total Mercury Analyses of The Sulphur Pool

	a	b	c	d	e	f	g	h	i	j	k	l
a						84	78	105	92	86		54
b						80	130	100	110	74		78
c			92	84	68	76	120	130	84	82		90
d		58	76	72	80	140	110		88	96	110	84
e				120	110	170	98		80	78	70	
f				96	110	120	82	68	78	76	88	
g				74	140	180	180	96	84	110	92	56
h				100	120	210	220	160	140	82		
i		64	180	160	210	340	360	280	410	340	84	78
j				88	100	160	220	180	950	280	94	90
k				42	140	120	180	240		110		86
l							140	260		320	96	102
m						130	280	320	380	120	76	
n				140	260	220	110	140	380	160		220
o	660	720	200	98			260	360	580	360	210	
p						78	35	142	213	64		
q					58		66	88	160	440	180	
r						130	110	580	460	720	260	150
s						180	240	400	660	320	480	1400
t								240	380	260	220	180
u										160	280	260

TABLE $(A.15)_e$ Total Mercury of The Tiger - Waima Area

	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t
a		600	1400	360		220	320	460	660									
b			1900	400	2800	580	1300	420	640	540	280							
c				150	3600	2200	1800	800	840	320	180							
d				220	5400	940	6600	1200	880	720	200							
e				460	380	400	2200	1400	1000	640	820	680	240	280	200			
f		120	300	280	440	700	180	2600	1100	520	7400	1600	329	540	220	240	120	
g		140	3400	2800	80000	420	160	720	260	1200	1400	2000	380	300	180	280	260	140
h		300	780	460	15000	780	660	340	380	440	740	110000	360	270000	260	120	130	86
i		260	480	420	600	720	3800	740	540	420	380	1820	940	860	720	340	220	100
j				140	180	280	480	580	360		340	460	540	580	420	120	160	90
k					180	100	120	700	320			180	220	280	120		92	
l				1600	120	220	600	520	140									
m						100	7500	1600	1100	180								
n						160	220	200	1500	800	220							
o								200	1200	240	100							
p									170									

TABLE (A. 16) FUMAROLIC MERCURY

Location	Flow l/min	Temp. °C	[Hg^o] µgm/l	Hg^o flux µg/min.	Flux subtotal
ZONE 1					
Waitotera Ponds	< 1	18	13	~ 0	
	5	20	15	75	
	25	24	20	400	
	35	30	32	1120	1595
Streams	⩾ 1½	18 - 19	0	0	0
ZONE 2					
Tiger Area	~ 2	18	~ 13½	~ 27	
	40	20	15	600	
	20	23	19	380	
	20	25	22	440	
	125	45	106	13250	
	50	62	276	13750	28447
Waima	~ 1	18	11	11	
	20	20	16	200	
	40	22	17½	700	
	50	25	24	1200	
	40	28½	29	1160	3271
Flat	20	22	18	360	
	5	24	20	100	
	30	27	28	840	1300
Mounds	5	21	16	80	
	20	22	17	340	
	20	26	23	460	880
Sulphur Pool	20	19	14	280	
	40	22	18	740	
	30	23	19	570	
	15	24	20	300	
	35	25	32	1120	3010
Domain	15	19	14	210	
	45	22	18	810	
	40	23	19	760	
	45	30	32	1440	
	½	39½	72	36	3256

TABLE (A.16) Contd.

Location	Flow l/min	Temp. °C	[Hg^0] µgm/l	Hg^0 flux µg/min.	
ZONE 2 (Contd.)					
Tuwhakino Pond	~ 2	18	14	28	
	25	21	16	400	
	30	26	25	750	1178
Waiapawa Pond	10	19	14	140	
	< 1	22½	19	0	140
Streams	65	~19	~ 14	930	930
ZONE 3					
Ngamakaikai Pond	10	19	14	140	140
Waiparaheke Pond	~15	18	~ 10	150	
	100	20	15	1500	
	40	22	18	720	
	50	23	19	950	3320
Sulphur Ponds	4	18	~ 8	32	
	25	20	15	375	
	20	23	19	380	
	25	24	20	500	1287

Total flux (µg/min) for all zones is 48.754

or 2.56×10^4 gm per year.

* Figures (A . 9) and (A .11) show the sites of fumarolic activity.

TABLE $(A.17)_a$ Analyses of Biotically Active Media (%)

	S	C1	Ba	Si	Ca	Na	K	Fe	A1
1	27.85	0.255	45.52	10.99	0.865	13.87	0.130		
2	33.35		65.60		1.05			0.163	
3	23.47		42.40	30.28	3.33		0.521		
4	21.79	0.453	60.55	3.316	0.664	13.15	0.073	0.155	
5	29.70	1.07	59.95	6.80				2.05	
6	17.75	13.51	53.10	4.26	2.49	8.50	0.394	0.272	
7	11.30	15.83	30.63	23.60	12.05	5.021	1.555		
8	9.74	29.42	31.94	13.08					
9	2.65	45.52	27.85	6.855	10.97		1.25	0.33	4.9
10*	51.52							46.29	
11*	56.45							45.86	

$(A.17)_b$ Element Ratios For the 'Biotic' Analyses.

	S/C1	Ba/S
1	109	1.64
2		1.97
3		1.81
4	48.1	2.78
5	27.6	2.02
6	1.314	2.99
7	0.714	2.71
8	0.331	3.28
9	0.058	10.5

* denotes mineral growing on the outer wall of the filamentous bacteria, and not of the medium in which it formed.

(The results were presented at the Carey Appreciation Symposium, 1977).

TABLE (A.18) Total Mercury in Geothermal Sediments (tonne)

Concentration (ppm)	Area (m^2)	Product*	Sub-Total*	Zone Total*
	CENTRAL ZONE			
	a. Tuwhakino			
92	6.7×10^4	1	10.25	
417	2.7×10^4	2	20	
467	1.4×10^4	3	12	
950	1.3×10^3	3.5	2.5	
765	1.6×10^3	4	2.5	
837	3.3×10^3	5	5.6	
2070	9.1×10^2	7.5	4.2	
2250	5.7×10^2	10	2.8	
1250	1.4×10^2	12.5	4.2	60
	b. Waiapawa			
12	3.2×10^4	1	0.6	0.6 61
	NORTHERN ZONE			
	a. Waitotera Ponds			
250	3.0×10^3	3	3.6	
15	10^2	2	0.30	
20	9.4×10^3	1	0.05	4_+ 4
	SOUTHERN ZONE			
	a. Waiparaheke			
65	4.5×10^4	1.5	4.7	
10	7.0×10^3	1	0.11	5
	b. Ngamokaikai			
20	$1. \times 10^4$	1	0.3	0.3
	c. Sulphur Ponds			
20	1.6×10^3	2	0.04	
28	1.2×10^3	2	0.055	
17	1.3×10^3	2	0.052	0.15 5

The total mercury held in the geothermal sediments of the Ngawha Basin = 70 tonne

* Unit(of mass) is tonne.

Table (A.19) SOIL CLASSIFICATION

(American Soil Orders and approximate equivalents in Great Soil Groups).

Order	Meaning	Approximate equivalents
1. Entisol	Recent soil	Azonal soils
2. Vertisol	Inverted soil	Grumusol
3. Inceptisol	Young soil	Some brown forest, gley
4. Aridisol	Arid soil	Desert, sierozem, solonchak, etc.
5. Mollisol	Soft soil	Chernozem, chestnut, prairie, rendzina.
6. Spodosol	Ashy soil	Podzols
7. Alfisol	Pedalfer (Al-Fe) soil	Gray-brown soil, degraded chernozem
8. Ultisol	Ultimate (leaching)	Red-yellow podzolic and reddish brown lateritic of U.S.
9. Oxisol	Oxide soil	Lateritic soils
10. Histosol	Tissue (organic) soil	Bog soils

Since 1965 this system has been the official classification system of the United States Department of Agriculture. The system is described in the U.S.D.A. Soil Classification, Seventh Approximation (1960).

TABLE (A.22) Radiocarbon Dating *

Sample No.	Description	Age Y.B.P. (with secular correction†)
CAD1 - 33	Tuwhakino area; Wood from Base of Lake Sediments near the Tiger Bath	38200 ± 1300
CAD2 - 84	Tuwhakino area; Cambrium, damp and semi-charred	6850 ± 150†
CAD3 - 82	Tuwhakino area; Outer trunk, damp semi-charred	6860 ± 110†
CAD4 - 82	Tuwhakino area; Interior wood, dry, semi-charred	6780 ± 90†
CAD5 - 459	Tuwhakino area; Loose Kauri wood in lowest 'thermal' horizon	7040 ± 70†
CAD6 - 162	Waitetera; exterior of buried in situ rooted trunk	24900 ± 1500
CAD7 - U.S.P.	Sulphur Pond; wet 'fibrous' exterior of buried trunk	1760 ± 60 †

* The determinations were done by the Institute of Nuclear Sciences, Petone, New Zealand in 1976 on samples supplied by the author.

TABLE (A.23) THE PROFILE DESCRIPTIONS

Each profile site has a two part description: the first is a general description of the profile locality, and the second describes the nature of the profile 'in situ'. The descriptions are included in the appendix following.

The format of the first part is: - profile number, name, geographical co-ordinates, relative elevation, parent material and form, slope, erosion, ground-water, geothermal acitivity, vegetation and human influence. Following this there may be a further comment on the area.

The second part is the description of the horizons in order of depth. In some instances the horizon thickness and depth are so variable that the approximate average depth interval is given. The descriptions include consideration of the following properties: thickness, moisture content, colour, mottling, stains, composition, sorting, shapes of grains, grain size, homogeneity, structure, compaction, rooting, hardness/firmness, fissility, plasticity, stickiness, porosity, permeability, odour, temperature, pH, gas, hydrothermal minerals and boundary nature. Where a comment is irrelevant, it is usually omitted: i.e. the property may be assumed to be 'absent' or 'normal': e.g. ambient temperature.

PROFILE A

N15/365346; 141.5 m; stream sediments, lake deposits and hydrothermal components; hard-capped mound; very pitted with mostly ragged outline; generally well bedded, overall subhorizontal to top with steep sides; erosion restricted by hard cap, some collapse of soft parts, water level is a few cm below base; virtually none on mound, slight activity at very bottom of profile; no vegetation, minor vegetation on adjacent mounds; small-scale mining has probably facilitated erosion of adjacent material and has taken material from the south-west side.

1. 0 - 18 cm; dry; $\frac{6}{2}$ 2.5Y greyish yellow poorly sorted silty coarse sand cemented by alunite; sulphur, dark organic remnants, haematite, cinnabar, ammaugnite and rare native mercury present, no roots; not compacted, porous, (except outer shell) fissile with effort, massive bed of dominantly angular grains; surface is a pitted hard-cap of virtually completely cemented sediments and low porosity,

the beds merge rapidly into:

2. 18 - 20.5 cm, faint dampness; $\frac{6}{4}$ to $\frac{5}{2}$ 10YR dull yellow or brown to mostly ca. $\frac{6}{3}$ 10YR, composition similar to above, but not cemented; loose, non-sticky, non-plastic, exceedingly crumbly; only minor alunite coatings.

merges into:

3. 20 - 25 cm; dry; $\frac{5}{2.5}$ to $\frac{6}{2}$ 10YR greyish yellow-brown, poorly ported coarse sand as in horizon 1; the alunite coating is thicker, and the clay content higher though minor, merges rapidly into

4. 23.5 - 27.5 cm; dry; $\frac{6}{2}$ 2.5Y to $\frac{6}{1}$ 10YR greyish yellow to brownish grey sediments as in A1, including more sub 0.2 mm grains than above centre of band is dominantly coarse sand, transitional (above and below); cinnabar rare.

merges into

5. 27.5 - 32.5 cm; dry; $\frac{6.3}{2}$ 10YR greyish yellow brown sediments as in A1; less coarse material than above, more vegetation debris and moist peat, towards the bottom the peat is dry and 'fissile'/crumbly; no visible cinnabar.

very rapidly merges to

6. 32.5 - 40.5 cm; damp; $\frac{4}{2.5}$ 10YR dull yellowish brown very silty sand; 'red-brown' leached wood fragments 5 cm, rare sulphur coated peat, poor compaction, loose, no cement, moderate sorting; peat near bottom is porous;

merges into

7. 40.5 - 53 cm; slightly damp; $\frac{5}{2}$ to almost $\frac{4}{2}$ 10 YR greyish yellow brown silty sand with some ca. 1 mm grit slightly larger amount of moist vegetation debris; plus minor charcoal; otherwise as above, merges into:

8. 53 - 64 cm; slightly damp; $\frac{5}{2}$ 10 YR silty fine-sand with wet darker silty, fine-sandy clay 'mottles', lenses rich in fine organic material (moist), and minor grit; grains are of high sphericity and roundness; significant peaty residue/stain on rubbing; few thin quartz-rich lenses, no hydrothermal minerals except rare sulphur; soluble iron present; in other respects very similar to previous layer merges into

9. 64 - 67.5cm damp to moist; $\frac{4.5}{2}$ 10YR, greyish yellow brown and very similar to above; has organic material, slightly grittier and an acid odour

merges with

10. 67.5 - 72.5 cm, damp to moist, $\frac{4.5}{2.5}$ to $\frac{3}{2.5}$ 10YR, ca. greyish yellow brown fine sandy silt, with rare angular grit; relatively compact, fair sorting, little cement; upper grains are partially alunite coated, lower grains completely coated, partially cemented and fissile; a few mottles of $\frac{6.7}{2.5}$ 10YR, dull yellow orange fine sand; otherwise similar to previous layer merges into

11. 72.5 - 89 cm, damp to moist; $\frac{3}{2.5}$ 10YR transitional to wet $\frac{5.5}{2}$ 10YR with depth; gritty sand with rare patches of paler fine sand near top, increase in grit (angular) and cement with depth, matrix is slightly finer at bottom; peat, charcoal, vegetation remnants, clay, sulphur occur in significant quantities throughout, plus some patches of dispersed haematite, ammaugnite and H_9S; strong D.M.S.O.* odour - particularly from wood; friable and loose to cohesive but neither firm nor non-sticky at bottom; relatively compact, no mottles, merges with

12. 89 - 114.5 cm, moist to wet, all organic material wet; mottly, dominant colours are $\frac{7}{2.5}$ 10YR, $\frac{4}{2}$ 7.5 YR and $\frac{5.5}{3}$ 10YR to $\frac{4}{3}$ 10YR sandy silts and sand with some $\frac{8}{2}$ to $\frac{8}{1}$ 5Y cemented sandy silt patch$_{es}$ in the upper part; considerable organic content, ca. 30% (charcoal, semi-charred wood and leached semi-charred wood), soft, not evenly distributed, thin sulphur on some wood, strong DMSO* smell; relatively compact; loose, rarely fissile, mostly crumbly with a slimy fine sandy feel; overall the layer is greyer near the bottom which contains a tilted large wet charred kauri trunk, (~6850 Y.B.P.)

rapidly merges into

13. 114.5 - 129 cm, dry to damp, $\frac{7}{1}$ to $\frac{6}{1}$ 10YR colour gritty and silty coarse sand, some cemented by sulphur and alunite; minor organic material; hard, where

cemented, mostly loose with moderate compaction, non-sticky.

merges into

14. 129 - 139 cm, damp to moist at depth, $\frac{6}{2}$ 10YR; ca. 3 cm band of 'sulphurised' grit passing into less sulphurous uncemented loose sandy grit, with local iron staining, little organic content for most parts. abrupt boundary with

15. 139 - 149 cm, dry mostly, intensely sulphurised carbon with minor other biogenic material, minor grit, traces of H_gS at top, hard, massive layer, fissile with much effort, brittle and very firm, subtle greyish mottles, apparently impervious to water(s) and gas. Basal 3 cm very rich in charcoal, up to 40%.

slightly wavy abrupt change to

16. 149.5 - 169+ cm, moist to wet, luke warm, $\frac{6}{3}$ YR10 (rarely $\frac{4.5}{3}$) dull yellow arrange to $\frac{6.5}{2}$ 2.5 Y at depth, where the subtle mottling wanes, well sorted fine sandy silt, very rare sulphur (only) as veinlets at top, no organic material, no 'obvious' iron staining, no cement, moderate compaction; some cohesion, but loose and very crumbly, non-plastic, non-sticky; very permeable to gas and water; some outbreak of slight gas (H_2S) activity.

Augering and nearby exposures indicate that this horizon continues well over a metre depth (stratigraphic), with only minor grain size variation. Correlation with the adjacent mound to the north indicates virtually undifferiatable sediments continue to depths over 3 metres below that excavated at site A.

*DMSO is dimethyl sulphoxide, which has a characteristic odour.

PROFILE B

N15/365345; 139.6m; reworked lake sediments and peat with strong hydrothermal influence; on flat in low-lying amphitheatre open to west; surface is horizontal to subhorizontal; water close to surface ca. 8-15 cm; mostly scattered minor gaseous activity; no vegetation except a central east-west tongue of bushy tea-tree; dredged for ore except tea-tree area where samples taken.

H. loose dry tea-tree leaves, damp in contact with ground, 2-3 mm deep.

1. 0 - 0.25 cm, variable; moist, ca. $\frac{2}{1}$ 10 YR humic with minor silt, slightly fibrous, loose, soft, poor compaction, hardly sticky.

rapidly merges into

2. 0.25 - 45cm; moist; $\frac{4}{1}$ to $\frac{3}{1}$ 7.5YR brownish black massive ? layered peat, some (variable) loose sediment on/near surface, rare superficial limonite, joints commonly cinnabar-coated; few roots penetrate to any depth; 'compacted' ; dense; firm to stiff to puggy, ca. non-sticky to moderately sticky, non-plastic to plastic, and damp to very moist with depth; not hard; no preserved organic remnants; oily odour, the few/rare sandy inclusions are usually cinnabar-rich, some near-surface peat has a cinnabar hue, ca. $\frac{4}{3}$ intensity.

merges into

3. 45 - 48 cm; very moist; $\frac{2.5}{2}$ to $\frac{3}{2}$ 10YR ca. silt; no coarse material thixotropic to puggy, mostly mobile plastic, fairly compact, adhesive rather than sticky; some sulphur (dispersed), merges with:

4. 48 - 135.5 cm, wet; $\frac{3}{3}$ 10YR transitional to $\frac{1.7}{1}$ 10YR and $\frac{1.5}{0}$ N silt, with small patches of $\frac{5}{3}$ 7.5 YR clayey silt, low down; no obvious structure; poor compaction, loose/ 'quick-silt' ; slightly puggy at depth, slight adhesion, possibly more heterogeneity with depth - minor fine sand, clay and organic material; strong oily smell, oil/tar coat grains, H_2S and Hg° present, warm, 37°C near bottom; orpiment 'vein' between 61 and 68 cm, irregular/sub-linear, 2 mm thick slurry; liquid mercury, e.g. 1 drop of 1.7 mm diameter at ca. 105 cm.

PROFILE C

N15/379349; 126.5 m at base, mat top; chaos breccia; slumping hillside adjacent creek; commonly 25-40°, locally steeper; lower $\frac{3}{5}$ of hillside suffers catastrophic slumping and erosion; water of pH 3.75 to 4.0 oozes from many erosion gullies, much of the subsurface is wet, but no general persistant water level exists; a few minor cold bubblings occur near base and in creek; tea-tree, and gorse scrubs dominate the areas without much erosion, a significant area is bare on the lower slopes; human influence is minimal except for some recently planted poplars.

H. rather sparse.

1. 0- ca. 40 cm, commonly ca 15 cm; dry to damp, $\frac{8}{2}$ 2.5 Y clay, relatively compact, firm to stiff and plastic, mostly crumbly/fissile, sticky when wet,

merges into

2. ca. 20-75 cm, commonly diffuse 10 - 20 cm thick band, damp to moist, $\frac{7}{4}$ 2.5Y 'light yellow' clay, poor compaction, granular tendency, loose, incompetent, very crumbly, slight stickiness, can be puggy to almost plastic and moderately sticky where wet; develops local small caps of limonite/haematite colouring, water from this layer is usually milky. merges into

3. ca. 35 - 350 cm, commonly between 40 and 250 cm; damp to very moist; $\frac{7.5}{3}$ 2.5 Y pale yellow clay highly incompetent; verges on a slurry where wet; very similar to C2 (above), but paler, and no iron-stains or reaction skins.

4. ca. 100 cm - commonly from below 200 cm; damp to moist, slightly variable colour in upper parts: $\frac{6}{10}$ 7.5 Y and $\frac{5}{1}$ 10 BG are the extremes, $\frac{6}{1}$ 7.5Y grey dominates; highly fractured shale, pelitic and calcareous; compact except for fractures, incompetent, extremely brittle/fissile, crushable by fingers, no stickiness, plain to faint mottling of iron-staining, fresh exposure may form a 'rusty' tarnish of $\frac{6.5}{4}$ 2.5 Y; fresh material may yield a sulphide odour on percussion.

Below ca. 300 cm rare limestone boulders occur erratically dispersed; these have usually $\frac{6.5}{4}$ 10YR dull yellow orange coating on the ca. $\frac{5.5}{1}$ 7.5 Y limestone (pelitic micrite); these boulders are hard, non-brittle, fracturing and competent, well rounded, sub-spherical and up to 1.5 m diameter.

PROFILE D.

N15/365347; 142.65 m; thermal pool - terrace deposits and lake sediments; terrace ending abruptly along the local drainage course, horizontal; erosion is minimal but for gradual collapse along steep banks; ground-water flows actively from below ca. 450 cm; recent Hg^{o} probably collected in some places due to diffusion and ground-water movement; ~~this becomes evident later in the thesis;~~ no sign of recent geothermal activity or minerals until 187 cm where historic activity indicated, at ca. 420 cm gas emission was able to commence, but is normally prevented by the overburden; healthy semi-mature tea-tree covers the terrace; human influence has been minimal.

H. Dominantly dry to damp tea-tree litter with minor braken, and lichen.

1. 0 - .5 cm, damp, ca. $\frac{1.7}{1}$ 10 YR virtually black, humic mat with traces of sand and silt, rarely 1.25 cm thick; minor compaction, soft, spongy, crumbly, virtually non-sticky, faint earthy odour, non hydrothermal associations, merges rapidly into

2. .5 - 3.0 cm, damp, $\frac{2.5}{1}$ to $\frac{4}{4}$ 7.5 YR browns, ca. $\frac{3}{3}$ 7.5 YR in bulk, (dark brown); humic material with minor quartz sand and silt; well rooted, slight matting, and some only partially decomposed debris; porous, soft, crumbly, non-sticky, non plastic; rare brittle small pieces of charcoal, rare firmer and moist clayey pockets, 16°C at bottom = air temperature. abrupt change to

3. 3.0 - 4.25 cm, moist, $\frac{1.7}{1}$ to $\frac{2}{1}$ 7.5 black clay with a few mottles to $\frac{4}{4}$ 7.5 YR brown; minor organic content, some roots, not compacted, massive, crumbly, non-plastic, soft, non-sticky; the browner mottles are compact, plastic, and very low in organic content. abrupt change to

4. 4.25 - 13.25 cm, damp, $\frac{5}{4}$ 7.5 YR dull brown very clayey silt with minor fine sand, few roots, relatively compact, crumbly with fair cohesion and firmness, little sticky; puggy/plastic wet; ca. fissile, dry to damp; elemental mercury condensate in adjacent joints and cracks. merges with

5. 13.25 - 28.5 cm; damp, $\frac{6}{5}$ 7.5 YR dull orange, clayey silt/silty clay, very few roots; bedding apparent (horizontal), fairly compact, sub-plastic, non-sticky, fair degree of crumbliness, firmish, earthy odour, rare root holes, slightly darker at bottom; a pale grey crust forms on exposure; elemental mercury also in openings.

rapidly merges with

6. 28.5 - 41.25 cm; faint dampness; ca. $\frac{6.7}{3}$ 10YR dull yellow orange clayey and sandy silt, no organic material, massive, faint fine horizontal banding; fairly compact, somewhat crumbly, sub-plastic, almost non-sticky, the few sandier sub-bands have poor cohesion; elemental mercury may occur in the few joints. merges with

7. 41.25 - 55.75 cm; damp to moist; $\frac{6.5}{6}$ 7.5YR orange motly silty clay with some ? peaty organic matter ($\frac{2}{2}$ 7.5 YR brownish black to black); very soft slimy on fingering and virtually wet, some associated 1 mm squares platelets of ammaugnite, ca. 0.5% v/v; compact, crumbly, partially sticky (? peat content); distinct layering, rare plasticity associated with the darker upper 8 cm and a 1 cm band ca. .5 cm above bottom. merges into

8. 55.75 - 60.75 cm moist to wet, ca. $\frac{5}{4}$ 7.5 YR dull brown, very clayey silt with minor sand; diffuse darker brown central band - ca. $\frac{3}{4}$ 7.5 YR mainly peat breccia, small soft pieces; compact, ca. plastic, slimy on fingering, slightly sticky merges into

9. 60.75 - 83.75 cm, damp, $\frac{6}{3}$ 10YR, dull brown sandy silt with minor clay, loosely held, poor compaction, non-sticky, very crumbly. merges into

10. 83.75 - 95.25 cm, damp $\frac{7}{3}$ 10YR dull orange silty fine sand with minor angular grit, no organic matter; massive non-compacted, very porous, loose/poor cohesion, non-sticky. merges into

11. 95.25 - 118.25 cm, damp, $\frac{6.5}{3}$ 10YR dull yellow orange banded sandy silt with rare peat; some compaction, fissile/crumbly, minimal stickiness, poor - fair cohesion, not plastic, homogeneous and massive; merges into

12. 118.25 - 132.25 cm, damp to slightly moist, $\frac{5}{2}$ 1.0 YR silty fine sand, greyish yellow brown with dark (black) mottly vertical striations (MnO_2 stains); otherwise similar to above. merges into

13. 132.25 - 158.25 cm, slightly damp, $\frac{6}{3.5}$ 7.5 YR dull brown silty fine sand, fairly well sorted, poor cohesion and compaction; very similar to above but less intense mottles. merges into

14. 158.25 - 186.75 cm, damp, ca. $\frac{6}{2}$ 2.5 Y (greyish yellow) grading to mottly $\frac{7}{2}$ 10 YR (dull yellow orange) with stains to $\frac{3.5}{2}$ 10 YR (brownish black) in lower 10 cm, fine sandy silt; poorly compacted, loose, faint stickiness, poor cohesion, merges rapidly into

15. 186.75 - 225.5 cm, dry to damp; $\frac{6.5}{3}$ 10YR dull yellow orange, slightly silty sand, very poor cohesion, no structure (all above are horizontally bedded) C^{o}_{2} type, very poor compaction - many holes up to .3 mm, no plasticity or stickiness, homogenous appearance; traces of possible hydrothermal minerals. merges into

16. 225.5 - 261.5 cm; distinctly damp. $\frac{6.5}{4}$ 7.5 YR dull yellow orange fine sand with traces of soft dark organic material, common dark mottly wavy striations; massive poor compaction, poor cohesion, non-sticky; strong oily odour; poorly discernable horizontal to sub-horizontal bedding fading to indiscernable with dark wavy mottles becoming broader and colouring entirely the last few centimetres.

rapidly merges against a Westward dipping surface

17. 261.5 - 290.5 cm, damp to moist, $\frac{6}{4}$ 7.5 YR dull orange, fine sand, with small particles soft black organic matter, and a few nodules of $\frac{3.5}{4}$ 7.5 YR brown silty clay up to .5 cm diameter; well-bedded, dip 27° west, subtle bending ca. 2 - 5 cm, vague darker mottles, poor compaction and cohesion, though some increase in firmness, variable faint stickiness - generally related to organic matter; pulverulent orpiment forming up to 1 mm grains, dispersed interstitially locallised about scattered centres, plus rare translucent red acicular realgar, ca. 1 mm long, tendency for larger numbers of grains near organic material. merges with

18. 290.5 - 308.25 cm; damp, $\frac{6}{3.5}$ 10YR, dull yellow orange sand with a trace of sticky clay; some widely dispersed dark organic material, poor compaction, slight crumbliness dominated by lack of cohesion, 27°west many clusters of acicular realgar, small amount of haematite in lower $\frac{2}{3}$ localised as concentric dispersions increasing slightly in intensity downwards. merges into

19. 308.25 - 336.25 cm; damp to slightly moist, $\frac{7}{3}$ 10 YR dull yellow orange sand, minor significant peaty material, minor grit, poor compaction, etc. as above; realgar common as small crystals, richest patches contain up to 5% realgar v/v; sulphur increases virtually replacing the haematite which disappears in the lower half.

merges with

20. 336.25 - 370.5 cm, moist; ca. $\frac{6.5}{3}$ 10 YR dull yellow orange sand with minor realgar oily grains in lower half; physical properties similar to above; sulphur slowly fades from near the top, iron rapidly increases then fades over 1.5 cm yielding to the more intense sulphur; sulphur alone coats the internal surface of the top of the fissure, ca. up to 1.75 mm thick, fissure (dormant/extinct) starts at 345 cm.

21. 370.5 - 398.5 cm, moist to very moist, ca. $\frac{6}{3}$ 10 YR to $\frac{2}{3}$ 10 YR, dull yellow orange to black, mottled peaty sand, paler parts are low in peat and drier, very minor iron staining locally a few cm from fissure, very minor alunite (weak cementing), yellow sulphur at and around immediate fissure, most grains are oil coated, fair compaction, verging on crumbly but still poor cohesion, non-sticky. merges into

22. 398.5 - 422.5 cm, moist to wet, $\frac{6.5}{3}$ 10 YR dull brown quartz rich silty sand; very similar to above, cakier on crumbling, weak Kauri oil odour, minor water seepage, no iron, very poor sulphur in top quarter of fissure, none below this

merges into

23. 422.5 - 434.25 cm, moist to wet; $\frac{4}{3}$ - $\frac{6}{6}$ 7.5 YR mostly $\frac{4}{4}$ 7.5 YR, 'orange' to dark brown mottly fine sand, dark wet peat up to 3 mm, oil and strong organic odours, massive, very poor compaction, sticky, non-plastic, fairly poor cohesion, minor thermal emissions soon broke out. merges into:

24. 434.25 - 455.75 cm, dominantly wet, $\frac{7}{3}$ 10YR dull yellow orange, and darker, mostly pale silty sand bands with rare peat; moderate compaction, no cement, poor cohesion, non-plastic, non-sticky; small dark bands/mottles containing fine soft organic, $Hg S$, Hg°_{l}, pH 4.5, 18.5°, to 28°, gas, H_2S, oil strong seepage of water with oil film, sand wet with oil is a brownish grey, faint D.M.S.O. odour at bottom; standing water level is from ca. 440^{+}cm, below which ground is fairly mobile.

25. 455.75 - 485.75 cm, wet, $\frac{4}{1.5}$ to $\frac{5}{3}$ 10YR brownish grey to dull yellowish brown as above, still bedded, plus much "wood" - mostly charred, and/or leached, very large pieces usually only externally charred; much oil, strong D.M.S.O. odour, Hg°_{l}, $Hg^{\circ}S$, H_2S, rare HgS coatings on wood; thermal activity became moderate causing collapse, maximum 29.5° C.

PROFILE E

N15/364347; 140.5 m; reworked lake sediments and organic debris; low terrace associated with thermal activity now eroded into by the streamlet from the Sulphur Pool, flat top and subvertical sides adjacent drainage; subhorizontal; groundwater is about 2.6 m below the top; geothermal emanations are widespread low-level gas percolating through the streamlet course and adjacent low-lying ground, only metres to the east-south-east the sediments have a high fossil hydrothermal mineral content; vegetation is dominantly tea-tree with minor gorse; human influence is minimal.

H. Up to 0.5 cm of litter, commonly 0.35 cm of tea-tree debris,

rapidly merges into

1. 0 - 6 cm, damp, ca. $\frac{2}{1}$ 10YR black humic clay, gradational to poorly humic at bottom, generally well rooted even band, somewhat fibrous at top, some compaction, loose, soft, non-sticky, non-plastic, no sign of hydrothermal activity.

transitional to

2. 6 - 13 cm, damp, $\frac{3.5}{3}$ 10 YR dark brown slightly silty clay, rarely humic, well rooted, earthy odour, some/fair compaction, soft, crumbly, non-sticky ca. non-plastic.

merges into

3, 13 - 31 cm, variable; damp; $\frac{5.5}{3.5}$ 2.5 Y yellowish brown as above, with faint signs of horizontal bedding; minor vegetation matter, few roots; some darker mottly patches, slight degree of stickiness.

4. 31 - 36 cm, variable; damp, $\frac{5}{3}$ 10 YR dull yellowish brown band of leaf rich silt, with minor clay, leaves are mostly flat lying; good compaction; strong cohesion perpendicular to bedding, to fair otherwise; crumbles into caky blocks with parallel faces to bedding ca. 1.25 cm blocks; some plasticity, slight stickiness, no roots.

rapidly merges into

5. 36 - 65 cm, damp to slightly moist; $\frac{4.5}{2}$ 10YR greyish yellow brown sandy coarse silt, no organic material, massive horizontal band, some small holes, ca. .3 cm,

evenly distributed, poor compaction, loose, no cementing, very poor cohesion, no stickiness or plasticity, odourless. abrupt change to

6. 65 - 97 cm, damp, $\frac{5.5}{3}$ 7.5 YR dull brown band of >25% vegetation debris, with a rapid transition $\frac{3}{5}$ of way down from leaves, with slightly increasing twigs, to layer composition of ca. 30% v/v trunks, branches and twigs, plus ⩾ 65% leaves; large logs are at the basal level; mostly compacted; where applicable crumbly into caky blocks (soft) of ⩾ 1 cm diameter and ⩾ .75 cm thick.

slightly variable abrupt change to

7. 97 - 160 cm, dry to damp, $\frac{6.5}{3}$5Y light greyish olive well sorted silt, no organic matter, massive horizontal band with no discernable fine structure, weakly cemented, relatively hard, very brittle and very fissile, fairly good compaction, no stickiness, signs of apparent hydrothermal attack and general iron/haematite staining, vaguely mottled, slight acid odour, slightly coarser grained near bottom. abrupt change to

8. ca. 160 - ca. 165 cm variable, dry $\frac{8}{1}$2.5 Y light grey pulveresent clay-like granular and powder with very minor "brittle" grit, no cohesion, incompetent, and loose, horizontal merges rapidly into

9. 165 cm - 239 cm, dry to damp, $\frac{7}{2.5}$ 2.5 Y (and some $\frac{7}{1.5}$ broad mottles at top) greyish yellow fine sandy-silt, no organic matter, massive, poor compaction, loose mostly, virtually no cement, non-sticky, no plasticity, incompetent, ca. odourless.

PROFILE F.

N15/366348; 146 m; lake sediments and peat; part of old lake floor, very subdued locally; 2 - 5° south-south-east to south-east towards thermal depression; minimal erosion, no groundwater encountered, probably close to bottom (93.5 cm), sign of current thermal activity, only a vague suggestion of weak historic activity - a few pale thin '? sulphurous' joint dustings; juvenile dense tea-tree; human activity has been minimal except for a down-slope track.

H. Thin humus cover, dominantly broken and tea-tree, with lichen and moss, relatively dry.

1. 0 - 2.5 cm, moist, $\frac{1.5}{0}$ N to $\frac{2}{1.5}$ 7.5 YR black mat of fine humic material, fairly well rooted, earthy smell but almost entirely organic, poor compaction, porous, crumbly/loose, virtually non-sticky, soft, merges into

2. 2.5 - 4.5 cm, moist to damp, $\frac{2}{1.5}$ 7.5 YR black fibrous organic mat with minor fine quartz sand, moderate rooting, very crumbly, porous, soft, poor compaction merges into

3. 4.5 - 12 cm, damp, $\frac{4}{2}$ to $\frac{3}{4}$ 10YR greyish yellow brown to dark brown very silty clay, some roots, quartz visible/handlens, earthy odour, soft, crumbly, relatively compact, porous, ca. non-sticky. merges into

4. 12 - 17.25 cm; damp, $\frac{4}{3}$ 7.5 YR dull yellowish brown mottled clayey silt with minor paler quartz sand lenses, minor roots, rarely compacted, to fair compaction, soft fissile/crumbly. merges into

5. 17.25 - 21.5 cm, ca. damp, $\frac{3}{3}$ 7.5 YR dark brown, basically as above, with a few ca. 1 cm clay patches - plastic; mottled and without roots; generally few roots. merges into

6. 21.5 - 26.5, moist, $\frac{2}{1.75}$ 7.5 YR brownish black silty clay, rare roots, poor to fair compaction, firmish, tends to be crumbly with little pressure - blocky lumps, tends to be plastic when moulded with care, non-sticky, silty feel on fingering, pseudo fissile dense merges into

7. 26.5 - 28.5 cm, damp to moist, $\frac{1.7}{1}$ 7.5 YR Kauri leaves in peat, bedded horizontal, tends to be crumbly, non-sticky except for slimy feel on fingering, virtually non-plastic; merges into

8. 28.5 - 38.0 cm, wet, $\frac{2}{1}$ 7.5 YR organic debris with some peat, debris is loosely held and partially decomposed; little/no compaction, crumbly/fissile to plastic, slightly sticky, slimy feel, almost odourless.

9. 38.0 - 40.5 cm, very moist to wet $\frac{2}{1.3}$ 7.5 YR black peat, minor debris, slimy feel, plastic, relatively soft, vague subtle mottling, paler where exposed or dry

merges into

10. 40.5 - 55.5 cm, very moist, $\frac{2}{0}$ N black dominantly, to $\frac{3.5}{3}$ 7.5 YR dark brown peat, no debris; fairly compact, soft, plastic, slimy feel, subtle paler mottles.

merges into

11. 55.5 - 83.0 cm, damp to moist, $\frac{4}{3}$ 7.5 YR brown gritty sand with some peat, moderate compaction, porous, crumbly to blocky fragments relatively fissile, leaving a dark brown sticky stain, dominantly non-sticky, virtually non-plastic.

merges into

12. 83 - 93.5 cm, very moist; very similar to 10, more compact, has $\frac{4}{3}$ 7.5 YR brown silty bands/lenses in lower part, ca horizontal.

PROFILE G.

N15/365347; 144.5; lake sediments and peat; just below the beginning of the depression about the Sulphur Pool, topography subdued; 3° - 7° west; erosion is minimal at site, minor surface accumulations occur in small downslope depressions; groundwater commonly emerges at ca. 120 cm, but deeper during prolonged absence of rain; no emissions at immediate site, nearby are minor gas emanations, activity steadily increases towards the Sulphur Pool, some earth (profile) is sulphurous, one sample left a mercury film on fingers; semi-stunted tea-tree covers much of the area except for a few barren patches; human influence is restricted to two downslope tracks, and the occasional fire.

H. Very little humus litter, rather patchy covering, occasional mixed-in sulphur.

rapidly merges into

1. 0 - .225 cm variable, generally .1 to .225 cm where it exists; moist, sharp well defined narrow band, $\frac{1.5}{0}$ N to $\frac{2}{1.5}$ 7.5 YR black mat of fine humic matter, moderate rooting, earthy to faintly acid smell, almost entirely organic, fair compaction, porous, crumbly to fine soft almost non-sticky 'granules', moderate cohesion.

rapidly merges into

2. .225 - 38 cm; moist; $\frac{2}{3}$ 7.5 YR very dark brown mottly and very silty clay, well sorted, some roots, rare organic matter, commonly poor compaction, but darker parts bare ca. good compaction (and probably contains appreciable peat), non-sticky to slightly sticky, soft crumbly/rare fissile tendency, poor plasticity; few thin diffuse edges of quartz silt ca. $\frac{7}{2}$ 7.5 YR light brownish grey, poor compaction, very fissile/crumbly, much less stickiness, rare sulphur though common nearby; no obvious structuring, possibly sub-horizontal. merges into

3. 38 - 67 cm; moist, $\frac{3}{2}$ to $\frac{4}{4}$ 7.5 YR brownish black to brown (transitional) clayey silt, minor and, some dark brown mottle where peat rich, no roots; compacted well, 'structureless', good sorting, soft, plastic, slight stickiness, overall crumbliness is fair; thixotropic lowest parts develop a tarry coating/capping on exposure.

merges into

4. 67 - 97 cm; moist to very moist, $\frac{4}{3}$ to $\frac{4}{2}$ dull brown clayey silt, with an appreciable peat content, faint D.M.S.O. smell, faint bedding, massive, compacted, plastic, soft, fairly sticky, not crumbly; develops a reaction skin of hard dark grey 'tar' with desiccation cracks. merges into

5. 97 - 115 cm, very moist to west, $\frac{3}{3}$ 7.5 YR dark brown passing into ca. $\frac{7}{6.2}$ 2.5 Y bright yellowish brown streams, peaty silt to silty and fine silty peat with sulphur, otherwise very similar to above. merges into

6. 115 - 125 cm, very moist, $\frac{3}{2}$ 7.5 YR brownish black peat with minor fine sand, very sulphurous (ca. $\frac{7}{6}$ 2.5 Y); unable to discern any structure, compact, plastic to thixotropic, soft, sticky, crumbles (with rapid movement) into ca. 0.3 cm pieces.

PROFILE H.

N15/364347; 140.3 cm; lake sediments partly reworked; small tableland (of old terrace) deeply dissected by watercourses; relative altitude above adjacent stream ca. 3 m; surface is horizontal to subhorizontal with subvertical sides by watercourses; apart from stream scouring and associated bank collapse, erosion is minimal; groundwater lies about 2.25 m below the surface; there is no current thermal activity nor any sign of past activity; tea-tree, some bracken, rare gorse; human influence is minimal.

H' Litter up to .75 cm deep, commonly .3 cm, fairly dry.

1. 0 - 4.5 cm, dry to damp, $\frac{3}{1}$ 2.5 Y brownish black transitional to $\frac{6}{3}$ 2.5 Y dull yellow in some lower parts; humus, wavy outline, broadly horizontal, minor fine sand, soft, friable/crumbly, not very matted, well rooted, porous, some compaction, tends to be darkest just above centre, some $\frac{6}{3}$ 2.5 Y zones have a poor humic content, generally clay content increases with depth. merges with

2. 4.5 - 7.5 cm, dry, $\frac{8}{3}$ to $\frac{8}{2}$ 2.5 Y light grey clay, some roots, fairly compact, fissile, firm, some crumbliness, "leached" appearance, merges into

3. 7.5 - 13 cm, dry to faintly damp; $\frac{7}{3}$ 10YR dull yellow orange to $\frac{6}{3}$ 2.5 Y dull yellow, variable, clay with some roots, moderate compaction, fairly loose, soft, no stickiness, some crumbliness but poor cohesion, dull earthy smell, slowly merges into

4. 13 - 34 cm; slight dampness; $\frac{5.5}{2}$ 2.5 Y dark greyish yellow fades to $\frac{7}{2}$ 2.5 Y greyish yellow clay, few roots, earthier smell no structure visible, fair compaction, very crumbly, relatively soft, non-sticky non plastic merges into

5. 34 - 39 cm; slight dampness, $\frac{5}{1}$ 2.5 Y yellowish grey and rapidly darkens to $\frac{4}{1}$ 2.5 Y, clay very similar to above, no roots, colour change probably due to boundary reaction abrupt change to

6. 39 - 41.5 cm, slightly damp, $\frac{4}{2.5}$ 10 YR greyish yellowish brown, silty clay band, very distinct upper and lower boundary though material below very similar, compacted, firm with some degree of softness, fairly crumbly, non-sticky, very poor

plasticity, band has a variable dip within 10 to 18° abrupt change to

7. 41.5 - 49 cm; damp to dry, $\frac{5.5}{4}$ 2.5 Y yellowish brown, silty clay, minor kauri debris - mostly leaves; poor to fair compaction, poor cohesion, soft and very crumbly non-sticky, non-plastic merges with

8. 49 - 52.5 cm dry, $\frac{6.5}{3}$ 2.5 Y "light yellow" slightly variable, as above except with some voids + some patches with considerable leaves lying along an irregular broken line, generally less cohesion than above merges with

9. 52.5 - 79 cm dry; $\frac{5.5}{3}$ to $\frac{6}{4}$ 2.5 Y dull yellow silty clay as per H8, perhaps more tree debris locally, the lower boundary is sharp dip ca. 14 - 17°, H6, H7, H8 and H9 form a single distinct "yellowish brown" layer; this abruptly changes to

10. 79 - c. 120 cm, dry; $\frac{7}{2}$ with minor $\frac{6}{3.5}$ 10 YR variable dull yellow orange beds of silty sands, no organic matter, mostly very loose, moderate compaction, very fissile, non-sticky, well bedded, dip ca. 30° to 35° (slight variations), no evidence of thermal activity past or present merges onto

11. ca. 120 - 190cm; damp; $\frac{7}{2}$ 10 YR dull yellow orange to $\frac{7}{1.5}$ 7.5 YR and 10 YR light brownish grey beds as above with ca. 40° dip between north north east and east; beds are more regular and some appear as narrow alternating bands ca. 2 - 6 cm thick, generally slightly darker near bottom.

PROFILE I

N15/363344; 173.1 m, chaos breccia; hillside; 10 - 15° north-east; ground appears not to suffer erosion - minimal for situation; no groundwater found; no obvious signs of thermal activity for 250 m, vegetation is mostly small tea-tree; human influence is minimal.

H. Very thin litter covering, scattered small areas with almost none, gorse is the main source. abrupt change to

1. 0 - 2.8 cm; dry to damp, rarely moist, $\frac{5}{1}$ 10 YR brownish grey fading rapidly $\frac{8}{2}$ 7.5 YR light grey clay with minor surface exposures of barren $\frac{8}{1}$ 7.5 YR light grey, very low humic content, some roots, compacted, soft to firm, plastic to very crumbly, mostly crumbly; rarely loose, generally sticky and plastic when wet merges into

2. 2.8 - 78 cm dry; $\frac{8}{3}$ plus minor $\frac{7.5}{3.5}$ 7.5 YR deeper, light yellow orange, clay, rare minor silt; mostly "compacted", but "fractured" well jointed 7.5 cm irregular blocks, firm, fissile/crumbly with effort, non-plastic, and non-plastic unless wetted.

merges into

3. 78 - 88 cm; dry, $\frac{7}{8}$ 10 YR yellow orange iron stained band of the above, the band is slightly wavey and has diffuse edges, the base of the band is transitional with the material below merges into

4. 88 - 320 cm dampt to moist, $\frac{8}{3}$ 7.5 YR light yellow orange with mottles of $\frac{8}{2}$ 2.5 Y pale yellow, below ca. 200 cm, clay with remnant texturing/pseudomorphing increasing with depth, all material present appears to be completely 'kaolinised', the apparently finer material tends to be more coloured, the finer material - the matrix lacks cohesion, poorly compacted, incompetent, and show only slightest plasticity and stickiness; the coarser clay lumps are very similar but display slightly more cohesion/more crumbliness, no roots.

PROFILE J

N15/364348; 144.5 m; peat, and organic debris and reworked lake sediments; terrace dissected by stream; flat horizontal surface and subvertical banks into stream; erosion of surface is minimal whilst banks are domated by collapse into the small stream; groundwater level is a few cm above the local stream, minor geothermal activity is confined to the stream, sulphur in the profile suggests some gas diffusion - none detected per se; well clad by bushy tea-tree, fairly open underneath; human activity has been minimal.

H. ca. 23 mm dry leaf debris, almost entirely tea-tree, generally overlying damp partially closely packed dark decaying leaves, up to ca. 5 mm.

1. 0 - 0.3 cm, moist, $\frac{2}{1}$ 10 R reddish black, very strongly humic containing decaying matter and very minor quartz silt; some compaction, nevertheless spongy, relatively non-sticky though adhesive, soft, friable, fairly well rooted, rare vertical holes, odourless, closely follows the surface merges with

2. 0.3 - 0.9 cm, slightly damp, 10R $\frac{5.5}{2}$ greyish red silty clay with darker mottles, a well rooted fairly fibrous mat, loosely held to relatively compact soft, fissile, silty feel on rubbing, non-sticky, non-plastic, no internal structuring. merges into

3. 0.9 - 5.9 cm, damp to moist, 10 R $\frac{2}{1}$ reddish black humic silty clay with small 7.5 YR $\frac{5}{3}$ dull brown mottles; many roots, structureless, moderate compaction crumbly smooth feel, some plasticity, earthy smell, soft, virtually non-sticky merges into

4. 5.9 - 7.4 cm, moist, 2.5 R $\frac{7}{1_3}$ light reddish grey silt/fine sand with minor dark peaty material with minor 10 R $\frac{3}{2}$ dark reddish brown organic rich patches, fair rooting, soft, fissile, slightly better compaction, firmer where paler, some crumbliness merges into

5. 7.4 - 12.4 cm, very moist, 7.5 YR $\frac{3}{4}$ dark brown to 10 R $\frac{3}{3}$ dark reddish brown silty sandy peat from kauri leaves, few roots, mostly compacted, soft, fissile and verging on plastic, sticky where finer grained; local concentrations of flat lying densely packed leaves, anisotropic firmness and very slimy feet, minor thin quartz sand band, relatively non-compacted, very porous, little cohesion, merges into

6. 12.5 - 50.5, damp, 10R $\frac{3.5}{3}$ reddish brown silty sand with moist to wet wood and leaves, rare thin lenses of paler sand, vague horizontal bedding, massive, mostly loosely held and very crumbly, good cohesion where organic rich, poor compaction, most organic rich zones are plastic, non-sticky. merges into

7. 50.5 - 80 cm, moist 7.5 YR $\frac{5}{4}$ dull brown fine quartz sand, some lumps of organic material, minor fine carbon, small irregular veins of dull yellow sulphur, near and below which wood is charred, moderate compaction, relatively loose, crumbly, D.M.S.O. smell, no roots merges into

8. 80 - 110 cm, moist to very moist where organic rich, $\frac{4.5}{3.5}$ 7.5 YR brown and with some wood, (more large pieces than above), some charcoal, well layered, siltier bands in lower half, thin sulphur coating in cavities, sulphur is $\frac{8}{3}$ 7.5YR to $\frac{8}{4}$ 10YR light yellow orange, moderate compaction, no cementing, soft, porous, crumbly; dark peaty streaks with stickiness noticed on fingering merges into

9. 111 - 141 cm, moist, $\frac{7}{3}$ 10 YR dull yellow orange where sandy to $\frac{2}{3}$ 10YR brownish black where peaty, dominantly well layered silty sand, sandiest at top, interlayered compressed leaves, fine silt in lowest layers, horizontal bedding, irregular sulphur veins and seams in the lowest 5 cm, some small logs; sandy layers are generally moderately compacted porous and crumbly; the silty and peaty layers have generally good compaction, low porosity and permeability rare thixotropic/plastic, to some degree with some crumbliness rapidly merges into

At the base of the above dip changes abruptly to 15 - 25° south west, variable dip, the unconformity corresponds to the base of the tree fragments, and to mildly mineralised zones further south.

10. 141 - 202 cm wet to very moist, clayey and peaty silty $\frac{3}{4}$ 7.5 YR dark brown with a few thin lenses of paler fine sandy silt, organic material rare, minor carbon dispersed throughout, sulphur filled joints permeate much of bed, slight dip change at 187 cm, well compacted, soft, plastic, slimy on rubbing, some mottling, mostly homogeneous, strong D.M.S.O. odour, tar and kauri oil (and their odours) also present. The first signs of current thermal activity broke out close to the base merges into

11. 202 - 267 cm, wet $\frac{4}{3}$7.5 YR brown silt with minor clay, much sulphur ($\frac{3}{4}$2.5Y pale yellow) as fillings, upper 20 cm wettest, cross bedding and irregular ripply lamelae, compaction good, puggy and fairly plastic, partially sticky grey mottles, H_2S, D.M.S.O. odours, H_2S and $H_g°$ readily detected. merges into

12. 267 - 287 cm, wet $\frac{4}{2}$7.5 YR greyish brown silty fine sand, few fine transitional laminations of slightly paler hues, very rare flocks of black organic matter, compacted, thixotropic to crumbly, virtually no sulphur passes into

13. 287 - 340 cm, augered, wet, $\frac{5}{1}$7.5 YR brownish grey, very rare sulphur, sorted silt, compact, no cement, slightly sticky, probably crumbly, oily smell.

J' 5 m upstream from profile J, same side of creem, very similar environment setting, ca. level of J8 and J9 dominantly J9:-

Massive densely packed band of kauri leaves, virtually no other material present not observed, mainly dry, damp at bottom where tar has formed, no sulphur, no hydrothermal activity indicated ~~figure (— . —)~~, thickness of leaf deposit is ca. 35 cm.

PROFILE K.

N15/365343; 159 m; chaos breccia; moderately steep hillside facing north-north-east and central thermal depression, about $\frac{2}{3}$ way down the hill; local slope is ca. 20°; erosion is not obvious; drainage is good, no groundwater was found; damp at bottom; no sign of thermal activity, vegetation is dominantly tea-tree, ca. 2 m high; human influence is minimal, main road is down slope ca. 5½ m away.

H. 1.5 - 2.5 cm of very loose litter, dominantly bracken and tea-tree.

1. 0 - ca. 4.5 cm, dry to damp; $\frac{3}{1}$ to $\frac{6}{2}$ 7.5 YR brownish black to greyish brown, mostly humic poor clay, well rooted at top and moderately fibrous transitional to rare roots in paler crumbly somewhat blocky clay, with good compaction; softish to firm, very fractured appearance, non-plastic, non-sticky. merges into

2. 4.5 - 17.5 cm, dry to faintly damp, $\frac{6}{1.5}$ 7.5 brownish grey to $\frac{7}{1}$5Y light grey clay; as above with no organic matter but rare roots; very blocky, ca. 1 cm. rapidly merges into

3. 17.5 - ca. 350cm, dry, $\frac{9}{0}$ N white to $\frac{8}{1}$ 7.5Y light grey columnar clay, 3.5 to 5 cm wide and up to 1 m high without a thin horizontal joint; compact with rare fine holes, fissile, very firm, neither sticky nor plastic unless wetted, rare pale iron stains. merges into

4. ca. 350 - 375 cm, damp, $\frac{7}{2.5}$ YR light brownish grey, slightly mottly clay, very poor cohesion, massive, fairly poor compaction, readily crumbled, variable aggregated - dominantly granules to small ca. 0.5 cm lumps.

PROFILE L

N15/366347; 140.2 m; reworked lake-sediments, ? stream sediments, organic debris and minor hydrothermal constituents; lower stream bank near profile D with intact beds containing vegetation debris, overlying lake sediments; variable slope, sub-horizontal to 40°, less steep slopes predominating; erosion is active by both the local stream and (general) weather; ground-water trickles slowly from the profile base; there is much small gas evolution in the adjacent stream, and considerable cinnabar, mercury, sulphur or/and "antimony" in parts of the profile; vegetation is non-existent, superficial collection of material for mercury extraction may have been carried out in the past, however there is no local evidence (on this side of the creek) at present.

1. 0. 0 12.5 cm, dry ca. $\frac{6.5}{3}$ YR dull brown silted, with surface remnants of semi-charred wood, charcoal, sulphur and minor alunite, common local hard caps of sulphur ($\frac{7.7}{6}$ 2.5 Y yellow to $\frac{8}{3.7}$ SY pale yellow); well bedded dip 12 - 15° north west, site has partial cap of dry hard sulphurised coarse sand containing minor carbon; poor compaction; little cohesion (no cementing), quite loose, no firmness, very rare fine sulphur grains. rapidly merges into

2. 12.5 - 27.5 cm, dry to damp; $\frac{6}{3}$7.5 YR dull brown, gritty and sandy silt, poorly sorted, contains minor charcoal; at the base there is abundant cinnabar and charcoal; well bedded; poorly compacted, virtually no cohesion though on rubbing there is a minor soft and slight sticky component (probably only sticky on rubbing), no firmness loose, merges into

3. 27.5 - 45 cm, dry, $\frac{5.5}{4}$ 10R reddish brown poorly sorted coarse sand with ca. $\frac{4}{1.5}$ 5P greyish purple bands, thincharcoaldominatedbands/lenses,cinnabarisabundant as the interstitial filling, poor cement is lenses up to 5 cm thick, and near the base is a thin band of dispersed dark purply red meta-stibnite (2 - 3% by X.R.F.) above a black laminated (? tangy peat and charcoal ??); the phyisco-mechanical properties are as in L2, with a slight increase in cohesion. Whole 'horizon' contains cinnabar and rare Hg^{o} l, rapid merges into

4. 45 - 80 cm, moist, $\frac{6}{3}$ 5Y to 7.5 YR dull orange to dull brown fine sand and silt with ca. $\frac{7}{1}$ 2.5 Y light grey minor grit, no conspicuous cinnabar; properties otherwise as above merges into

5. 80 - 110 cm, damp to moist, $\frac{3.5}{3}$ 5YR dark reddish brown silt band with poorly defined bands and laminations, contains much charcoal, peat (wet) and sticks; fair compaction, soft, poor cohesion though somewhat plastic/crumbly, a few puggy zones, mostly sticky merges into

6. 110 - 170 cm, moist $\frac{5}{3}$ 5YR dull reddish brown fine sand, 'structureless', no carbon present (some exists to east of profile); some greyer mottles, and slightly browner where exposed; other physical properties as per L 4; merges into

7. 170 - 210 cm, moist to wet, $\frac{4}{3}$ 7.5 YR brown fine sand, with some $\frac{6}{3}$ 7.5 YR dull brown silt bands; sandy parts contain cinnabar and are commonly coated with a liquid mercury film, rarely does mercury metal invade the silt; exposures are haematite, jarosite, or rarely, tar capped; no organic remnants appear in the horizon; moderate compaction, crumbly, slight stickiness, no internal cement, slightly oily, Hg^{o}_{I} stains are common near the foot of this layer on adjacent ground where water has come from this profile.

This horizon is not directly below the above, it stratigraphically underlies seven but is displaced 7.5 m east south east to keep water influence minimal:

8. 210 - 225 cm, moist, $\frac{4}{2}$ 10 YR greyish yellow brown sand with $\frac{4}{2}$ to $\frac{4}{1.5}$ 7.5 YR brownish grey silt, no carbon, rare "veins" of haematite, very rare surface limonite, no obvious cinnabar, similar properties to above, possibly less oily.

PROFILE M.

N15/364345; 149 m; lake beds; local non-depressed area of lake basin, general vicinity sample of site has little relief, but relative to the broader scale, the area is ~ 10 m higher than the nearby Tuwhakino Stream towards which there is a variable incline; subhorizontal; erosion is minimal; ground-water was not reached; no sign of geothermal activity, past or present; fairly healthy tea-tree scrub; minimal human influence locally, though only 80 m from old ore stack - however drainage from this stack does not approach the sampling site.

H. Thin cover of tea-tree leaves ⩽ 1 mm, and lichen.

1. 0 - 3 cm, damp, transitional from $\frac{3}{2}$ 7.5 YR mottly brownish black with lesser $\frac{5}{4}$7.5 YR to $\frac{4.5}{2}$ 7.5 YR fibrous clayey humus to humic clay; no obvious pervasive structure, well compacted, softish but firm, crumbly, non-sticky, well rooted, contains minor silt merges into

2. 3 - 4.5 cm, damp, $\frac{4.5}{4}$ 5YR to $\frac{5}{3}$ 7.5 YR, dull reddish brown the dull brown silty and slightly humic clay, well rooted, fairly well compacted, firm crumbly, minor fissility, non-sticky, non-plastic rapidly merges into

3. 4.5 - 6.75 cm, damp, $\frac{5}{3}$ 7.5 YR dull brown, silty clay; very similar to above, except poor rooting and a few small irregular shaped holes, rare stains from above, merges into

4. 6.75 - 8.5 cm, damp, ca. $\frac{4}{6}$ 5YR reddish brown silty clay, few roots, some colour penetrates from the surface; similar M3, and slightly firmer.

fairly rapid transition to

5. 8.5 - 36.5 cm, damp, $\frac{8}{2}$ 7.5 YR light grey silty and slightly sandy clay with$\frac{6}{3}$ 7.5 YR mottles (dull brown); very few roots, fairly compact, massive, firm, crumbly, non-sticky, very poor plasticity, ggenerally siltier than above, merges into

6. 36.5 - 39 cm, damp+, $\frac{5}{3}$ - $\frac{5}{4}$ 7.5 YR dull brown silt band with diffuse edges, ca. 3° dip ~ north-north-west, fairly well compacted, fissile and crumbly non-plastic,

non-sticky, merges into

7. 39 - 49 cm, moist, $\frac{4}{3}$ - $\frac{6}{4}$ 7.5 YR brown to dull orange fine sandy silt, massive, no fine structuring, palest at very top, similar properties to above

merges into

8. 49 - 65 cm, moist $\frac{4}{3}$ 7.5 YR brown, faint mottling, dominantly silt but has grit present in variable small proportions; very base contains some kauri leaves, otherwise similar to above.

PROFILE N.

N15/373334, ca. 151.6 m; lake sediments; half way down a small rise in old basin floor; subhorizontal, erosion is minimal; groundwater level was found at ca. 2.9 m; no sign of geothermal activity; dominantly gorse with minor tea-tree and bracken; human influence is confined to some recent small excavations for sand some distance away and down-slope.

H. Gorse with mostly gorse, minor tea-tree and bracken litter, probably a fire in recent past. abrupt change to

1. 0 - 9 cm, dry, $\frac{3}{1}$ - $\frac{2}{1}$ 10YR brownish black humic clay, with minor silt passing into coarser sediments - poorly sorted; fibrous tendency at very top, moderate compaction, firm and crumbly to 2 - 3.5 cm blocks, non-sticky, medium to poor rooting; occasionally baseline extends down top 45 cm, irregularly merges into

2. 9 - 50 cm, dry, $\frac{6}{3}$ 7.5YR/5YR dull brown, from $\frac{4.5}{3}$ 7.5 YR brown, patchily mottles and partially kaolinised sandy silt; some compaction, firm, crumbly/fissile, non-plastic, non-sticky; some irregular jointing, granular nature blocks merges into

3. 50 - 75 cm, dry, variably coloured patches, mostly ca. $\frac{3.5}{2}$ 5YR dark reddish brown poorly sorted sediments, clayey and silty sands, less clay toward bottom, ~ no kaolinisation, minor compaction, extremely friable, very little cohesion, only minor stickiness from clay fractions - not "en masse", no roots. merges into

4. 75 - 230 cm, dry to damp at depth, bands of ca. $\frac{5}{4}$ 7.5YR dull brown poorly sorted silty sand and coarse sand, with two distinct narrow bands of $\frac{7.5}{4}$ 10YR dull yellow orange sandy silt, ca. 1 and 3 cm thick; generally bedding is vague, dip 15° south west; poor compaction, very porous, very crumbly, non-plastic, non-sticky, wet at very base - standing water level.

PROFILE 0a

N15/377338; 145 m, recent lake deposits of surrounding material including a large amount of organic debris; lake shore; and near shore bottom, gentle slope into lake; deposition environment mostly; lake level; ~ 5 cm below sampling site, widespread minor small gas vents, variable density; no living vegetation; human influence minimal.

1. 0 - ca. 3 cm, commonly between 2 - 5 cm depth; moist, $\frac{3.5}{4}$5YR dark reddish brown silt plus minor peat, some lamination below 1 cm; no compaction, no cohesion, some sticky material except at surface, non-sticky overall, rare colloidal sulphur locally merges into

2. ca. 3 - ca. 7.5 cm, highly variable thickness, rarely missing, wet, $\frac{6}{5}$2.5 Y bright yellowish brown sediments as above plus sulphur dispersed throughout; some silty sand plus sulphur, lower rapidly merges into

3. ca. 7.5 - ca. 22.5 cm; variable thickness, $\frac{3}{4}$7.5 YR dark brown, very little compaction, poor cohesion, incompetent "slurry"; partially weakly sticky (probably the organic compennet(s)), merges into

4. from ca. 22.5 cm (and as shallow as 15 cm) to over 1.25 m, wet $\frac{3}{4}$7.5 YR dark brown to between ~ $\frac{2}{2}$ 7.5 YR brownish black and rarely ca. $\frac{5}{5}$2.5 Y yellowish brown silt to peaty silt with much kauri debris from leaves to trunks, some sulphurous patches mostly in upper one third, below this is "vein-like" fillings mostly; in lower half there is a steady increase in peat though not quite to the dominant phase; facies logs in lower 2/3, generally point down into lake, some consolidation, puggy/mobile plastic, weakly sticky, peat is sticky, debris and peat cause cohesion, logs.

The thermal activity was caused to break out near the top of the layer, weak, CO_2 dominated, rarely H_2S rich, Hg° readily detected, pH ~ 4.3.

PROFILE Ob (& Oc)

N15/376338; 146.4 m; fluvial deposits including organic debris from nearby - this includes material of "lacustrine" and chaos origin; terrace, near lake; subhorizontal; minimal; variable - many parts are still swamp, local site fairly well drained, water level same as lake -2.80 m; local minor gas evolution, rare associated sulphur, much sulphur low in profile; vegetation is scarce, and mostly stunted, at site none; human activity is minimal generally, except for a recent drainage canal from start of the swamp into the lake.

Ob

H. Very poor at best to north side of canal and a general poor cover to the south west. Near the canal mud lake much of the north eastern ground is barren with old tree remnants on the surface, some sulphur occur at surface here,

abrupt change rapidly merges into

1. 0 - 0.5 cm, dry, $\frac{2}{1}$ 2.5 Y black 'crust' with desiccation cracks, hard, brittle, humic, not earthy; (soft, slippery when thoroughly wetted - where possible); no roots, compacted, apparently no sediments, probably highly organic, with possibly clay. This material does not cover more than ca. 35% of the ground locally.

abrupt change to

2. 0.5 - 60 cm, dry, locally damp, $\frac{6}{3.5}$ 7.5 YR dull brown silty clay, well sorted, massive, vague horizontal and subhorizontal bedding, roots rarely penetrate any significant distances, well compacted, very firm, crumbly/fissile, non-sticky, non-plastic, slightly coarser grained at depth; wavey (irregular) baseline, average horizontal, rapidly merges into

3. 60 - 195 cm, dry, $\frac{7}{3}$ 10YR dull yellow orange gravelly sand, with a high silt content except between ca. 197 - 202 cm where the horizontal is very loosely held, bedding not discernable, though there are semblances of broad scale horizontal changes poor cohesion and compaction, extremely crumbly, incompetent merges into

4. 195 - 235; essentially as continuation of the above; dry, $\frac{7}{2.5}$ 10YR dull yellow

orange, has minor cementing by alunite, iron, and very minor sulphur; a reaction skin of alunite and/or haematite develops in exposures: alunite occurs higher in profile than haematite; darker and damper near bottom last 20 cm; merges into

5. 235 - 242.5 cm, damp, $\frac{5}{1}$ 10 YR brownish grey to mostly $\frac{3.7}{1.5}$ 2.5 Y dark greyish yellow, sulphurous coarse silts to sand, fair sorting, well-bedded, not firm, poor cohesion, non-plastic, non-sticky, with slight adhesion, some wood at bottom; rapidly merges into

6. 243 - 285 cm, moist, $\frac{2}{1}$ to $\frac{1.7}{1}$ 2.5 Y black (matrix) peaty silt to silty peat, with large proportion of forest debris, including whole trees, sulphur may occur throughout vertical section, patchily or not at all, peat exceeds 75% v/v of bottom few cms; generally the peat has a "blocky" appearance, i.e. has probably been broken up; mostly well compacted, soft to occasionally firm, puggy to plastic, sticky, not mottled, in lower half vegetation debris declines, and there are some rare occurrences of goethite - including one 1.5 kg nodular filling.

Oc

As for Ob, but 5 m west near stream.

H. Very poor litter, vegetation commonly sparse, to patchy stands of tea-tree to south west tea-tree yields to dense gorse. Rarely sulphur at surfaces in hard lumps up to .5 cm.

1. 0 - .5 cm, dry, $\frac{2}{1}$ 2.5 Y black 'crust' with desiccation cracks, only a partial covering; compact, hard, very brittle, not earthy, no coarse material, no roots; rare sulphur; when wetted and worked, is soft and slimy, probably organic.

abrupt change to

2. 0.5 - 135 cm, dry $\frac{6}{3.5}$ 7.5 YR dull brown silty clay and clayey silt, fairly well sorted, massive, with vague horizontal bedding, some subhorizontal, well compacted, very firm, fissile/crumbly, non-sticky, non-plast rapidly merges into

3. 135 - 165, dry to damp, $\frac{4.5}{2}$ 2.5 YR dark greyish yellow massive, featureless, well compacted, very clayey silt; very firm, crumbly to verging on stiff plastic, faint stickiness abrupt change to

4. ca. 165 - 167 cm, ~ constant thick, but gently variable depth, $\frac{2.5}{1}$ to $\frac{1.7}{1}$ 10YR black charcoal band, compacted small pieces up to ca. .75 cm, soft, poor cohesion, crumbly abrupt change to

5. 167 - 207 cm, damp to dry, $\frac{6}{3}$ 5YR dull orange fine silty clay, massive and almost featureless but for some irregular jointing, and increase to minor sulphur content in the lowest 3 cm, compact, 'hard', crumbly with difficulty, non-sticky merges into

6. 207 - 213, moist, $\frac{5}{2}$ 10YR in dominantly $\frac{3.7}{1.5}$ 2.5 Y coarse silt; very sulphurous, and contains some sand and silt, bedding well defined; fair compaction, soft and slightly plastic, not sticky.

7. 213 - 253, wet, $\frac{2}{1}$ to $\frac{1.7}{1}$ 2.5 Y clayey silt with some sand grading to peat containing a high proportion of tree debris, (leaves to trunks) some sulphur - though variable, well compacted, generally plastic, soft and loose - to puggy, rarely firm

PROFILE P

N15/384355; ca. 179.8 m; chaos breccia; steep hillside with catastrophic collapse and earth flows; subhorizontal at top to vertical and subvertical sides facing the Ngawha Stream; erosion is "massive" and mostly due to movement of incompetent "bedrock"; ground-water oozes from the base of the slip only in small quantity, water-level is that of the creek, no geothermal activity noticed; except for a single minor bubbling a little upstream from the slip area; vegetation ranges from pockets of relatively juvenile kauri forest to dominantly tea-tree scrub, much of the slip area is devoid of vegetation; human influence is probable non existant in the vicity of the slip.

H. Litter is patchy in neighbouring area, none to a few cm deep locally in fissures, commonly .2 to .3 mm where tea-tree clad rapidly merges into

1. Rare 0 - 0.15cm, damp, $\frac{3.5}{1}$ 10YR brownish black humic clay, weakly fibrous mat, with very minor silt to clay rapidly decreasing in humic content, poor compaction soft, non-sticky, non-plastic, moderately well rooted, porous, merges into

2. ca. 0 - ca. 6.50 cm, damp; $\frac{8}{1}$10 YR light grey clay, commonly $\frac{6}{2.5}$2.5 Y greyish yellow at top; structureless except for slump cracks, moderate compaction, massive, generally firm, somewhat sticky, plastic to very crumbly, poor rooting mostly merges into

3. ca. 600 - ca. 850 cm, damp, $\frac{7}{3}$10 YR dull yellow orange clay as above, and less firm, slowly grades overall into incompetent clay pseudomorphs of rock fragments merges into

4. ca. 650 - 10,000 cm, damp to dry; various shaes of mid-grey shale, mostly ca. $\frac{6}{1}$5Y and $\frac{6}{1}$2.5 Y; $\frac{6}{1}$10 G, $\frac{5}{1}$10 G and $\frac{5}{1.5}$10 BG less commonly, generally not mottled colour variations are prevalent in older near surface exposures, very fresh material has the least yellow component; very rare sulphide odour on percussion, less iron staining and less frequent limestone boulders than at site C, pelitic shale, calcareous, massive, structureless, "homogeneous", incompetent, extremely fractured, brittle - pulverable by fingers, no plasticity, no stickiness, poor cohesion, compacted, "hard" fragments range from dominantly sub 1 cm "fracture" faced lumps downwards.

PROFILE Q

N15/386344; 132 m; basalt flow; flat plain, horizontal to subhorizontal; minimal; not encountered; no sign of activity, past or present; thick gorse with some grasslands; used for cattle - sampled area inaccessable to cattle and not treated for agriculture, several fires in past.

H. Litter from dense gorse cover.

1. 0 - .5 cm, dry to damp (mostly), $\frac{2.5}{2}$ to $\frac{3}{2}$ 10YR brownish black, well rooted, silty humic matter, very loose and porous at top, usually not matted, soft, very little compaction, fairly crumbly, no plasticity, slight stickiness. merges into

2. 5 - 40 cm, damp to moist, transition from above colour to paler then dominantly $\frac{4}{1.5}$ to $\frac{5}{2}$ 2.5 Y dark greyish yellow clay, crumbly and slightly plastic, firm, moderate compaction, some stickiness merges into

3. 40 - 52.5 moist, ca. $\frac{5.5}{4}$ 2.5 Y dull yellow clay, good compaction, firmish, plastic, moderate stickiness - stickier if wetted, poor crumbliness, no mottles fairly rapidly merges into

4. 51.5 - 57 cm, moist, between $\frac{7}{5}$ 10 YR bright yellowish brown and $\frac{6.5}{4}$ 2.5 Y dull yellow clay, excellent compaction, firm, stiff plastic, slight stickiness - sticky if wetted, no crumbly, mottly near surfaces, rare 'sandy' component felt on rubbing, passes rapidly into basalt which has a 0.2 to 1.5 cm weathered rim, scoriaceous where fresh.

PROFILE S

N15/371340; 143.1 m; probably chaos breccia; swamp plain; horizontal; none - save by leaching; saturation, standing water-level at ca. 4 - 5 cm below surface; tea-tree; negligible human influences.

1. 0 - 20 cm, moist to wet, $\frac{2}{1}$ 7.5 YR black to $\frac{2.5}{2}$ 7.5 YR brownish black, humus, peat, wood and organic debris; mostly well rooted, fairly compact, soft, moderate stickiness, puggy, only slightly sticky or plastic at top. merges into

2. 20 - 25 cm, wet $\frac{3}{1}$ 5YR brownish black humic rich clay, very minor silt, no roots, compact, sticky, puggy, structureless diffuse edged horizontal band, some firmness, slight mottliness at top, some roots merges into

3. 25 - 55 cm, wet, $\frac{5}{1.5}$ to $\frac{5}{2}$ 5YR greyish brown silty clay, "humic" stain fading with depth and rapidly disappearing at base to ca $\frac{6.3}{1.5}$ 5 YR brownish grey, horizontal horizon, compact, soft, puggy, sticky, no mottles, no roots merges into

4. ca. 50 - 175 cm, wet, $\frac{8}{3.5}$ 7.5 YR light yellow orange clay, slightly gritty feel towards bottom, fairly compact, puggy, 'wetter', incompetent, tends to flow/thixotropic, very sticky, no mottles; less sticky, tendency to crumbly and slightly firmer at very bottom.

PROFILE T

N15/364344; 140.2 m; dominantly lake sediments, probably minor chaos and hydrothermal constituents; stream banks; variable slope 4° - 15°, mostly about 5°, site ca. 5°; eroded by creek, weather and probably historic thermal ebullience; water level ca. 30 cm below surface until at creek level; local geothermal activity slight, otherwise in an area of widespread moderate to vigorous activity; no vegetation; area was once dredged for mercury ore (above this surface), current human activities minimal.

1. 0 - ca. 13 cm, moist $\frac{4}{4.7}$ 7.5 YR brown to $\frac{2}{2}$ 7.5 YR blackish brown silt with peat, wood, charcoal, sand and kaolin lumps, moderate compaction, somewhat crumbly/dominantly plastic, firm, slight stickiness, faint D.M.S.O. odour, no roots (possibly some remnants), no obvious bedding, some mottling, generally darker below first 0.75 cm; overall resembles a heterogeneous breccia/conglomerate rewelded by silt

rapidly merges into

2. 13 - 31 cm, wet, $\frac{3.5}{2}$ 2.5 Y yellowish grey tarry/oily loose sand, poor sorting, and compaction, very little cohesion, minor stickiness - due to oil only, ~ homogeneous, pungent organic odour, minor Hg^{O}_{l}, warm, generally not much fine grained material

merges into

3. ca. 31 - 45 cm, very moist, $\frac{3}{7}$ 7.5 YR brownish black to $\frac{4.2}{1}$ 7.5 YR clay and silty clay, minor rounded ca. 1 cm $\frac{7}{1.5}$ 10 YR light grey kaolin, black organic matter (soft), (peat and wood), kauri leaves, no discernable structure; plastic to almost mobile, not very sticky, poor cohesion, fair adhesion.

Strong hot ebullient/semi-ebullient geothermal activity uncontrolably breaks out near the bottom of this making it impossible to continue. Similar ground to the above occurs all around the Tiger Bath, High Tiger, Small Tiger, Waima and some ground between them - especially where low-lying. Waima and the Small Tiger have loose dull brown sand covering similar material, generally Waima lacks firm uppermost horizon; the layer is replaced by one which has a slightly sandier matrix, smaller "breccia"/conglomerate fragments and much less competence.

PROFILE U

N13/361344; 175.3 m; chaos breccia; locally fairly steep hillside not far from creek; 25 - 40°; most erosion by earth flow, rapid removal of surface material, no free groundwater found; no sign of geothermal activity; vegetation is a little variable in density, mostly tea-tree and bracken; human influence small, possible increase in earth-flow due to road-cutting below site.

H. Dry bracken and tea-tree little - variable 2 - 5 cm deep; mostly a complete cover (nearby cover is usually ≤ 1 cm) decay starting at bottom.

1. 0 - 3.5 cm, damp, $\frac{3.5}{2}$ 7.5 YR brownish black transitional to $\frac{5}{1.5}$ (and rarely $\frac{7}{1.5}$) 75 YR greyish brown humic and slightly silty clay, dominantly fibrous surface; low compaction, soft, crumbly, some firmness and plasticity, where humus thin, porous, non-sticky, well rooted rapid mergence into

2. 3.5 - 18.5 cm, slightly damp $\frac{7}{1}$ - $\frac{8}{2}$ 7.5 YR light brownish grey fading to light grey clay, with rare $\frac{6.5}{2}$ 10 YR greyish yellow brown penetrating from above, compacted, firm to hard, many joints, ca. rectilinear, causing blocky appearance (1 - 2 cm wide), crumbly/fissile, mostly non-plastic and non-sticky (except if wetted), poorly rooted irregular rapid mergence into

3. ca 18.0 - ca. 80 cm, damp to moist; mostly ca. $\frac{8}{1}$ 7.5 YR light grey clay minor brownish grey mottles, virtually no roots, very similar to above but sub-columnar to columnar jointing.

4. 80 - ca. 155 cm, moist, some damp, $\frac{8}{2.5}$ 7.5 YR light yellow orange clay, kaolinised chaos, very "fractured"/brecciated, incompetent, poor compactness, readily crumbled to faintly sticky powder, fine up to some pebble sized clay agglomerates, very irregular lower boundary; ranges from dominantly a rapid transition to a gradual mergence into

5. 185 - 365 cm, damp to moist, $\frac{6}{1}$ 10 BG bluish grey with common iron staining mottles - $\frac{5}{1.5}$ 5Y greyish olive, massive pelitic shale; incompetent, compacted, very brittle breccia, very similar to above except no clay and harder, rare sulphides small on percussion of fresh dry bluish grey samples.

PROFILE W

N15/362362; 148.1 m; probably chaos breccia dominantly or Cretaceous sediments, minor lake sediments; low-lying subdued area near Pond; subhorizontal; erosion by weather fairly active; ground-water level not encountered even below pond level; no current activity, some indications of past activity; no vegetation; very little human influence - rare wandering stock.

1. 0 - 9cm, damp, $\frac{6}{2}$ 10 YR greyish yellow brown very clayey silt, minor fine organic matter, no roots, silt is dominantly quartz; few very thin lenses of silt (friable), minor cementing, rare thin alunite joints fillings/coatings, dispersed fine grained cinnabar - least at very top which is $\frac{6.5}{3}$ 10 YR 7.5 YR bright yellowish brown, well compacted, firm to very firm, crumbly/friable, non-sticky, non-plastic, scarcely mottled, dull kauri oil smell merges into

1. 9 - 19.5 cm, damp, $\frac{5}{2}$ 10 YR greyish yellow brown, clayey fine silt, very firm plastic, non-crumbly, can be shattered into semi-conchoidal fragments, non-sticky, no obvious organic material, well dispersed minor sulphur, very well compacted. merges into

3. 19.5 - 35, damp to moist, $\frac{5}{2}$10YR/2.5 Y dark greyish yellow, similar to above, has obvious minor sulphur, and rare scattered pebbles commonly angular, slight friable tendency - with difficulty slightly finer matrix, forms green iron minerals (2°) on exposure, ease side like west side of Waiparheke only darker merges into

4. 35 - 50 cm, slightly moist, $\frac{4}{2}$ 10 YR greyish yellow brown, very similar to W2, possibly siltier, less sulphurous and only in small patches.

5. 50 - 60 cm, slightly moist, $\frac{3}{2}$ 10 YR brownish black, minor $\frac{4}{2}$ 10 YR (as 4), minor sulphur mottles, firmer, than above.

6. 60 - 70 cm, slightly moist $\frac{4}{1.5}$ - $\frac{4}{2}$ 10 YR greyish yellow brown clayey silt, as above, sulphurous mottles of $\frac{6}{3.5}$2.5Y dull yellow merges into

7. 70 - 85 cm, damp to slightly moist, $\frac{3.7}{2}$ 10 YR greyish yellow brown clayey fine grained silt, minor sulphur rich lensoidal bands of coarse silt - $\frac{7.5}{6}$ 10 YR/2.5 Y

bright yellowish brown; very firm plastic, non-crumbly, slight stickiness, very well compacted, except for minor porosity in sulphurous lenses, rare small vesicules ca. $\leqslant$ .05 cm, odourless, no organic material, no geothermal activity broke through, (faint ly) luke warm (cold day).

PROFILE X

N15/365364, 140.1 m, fine lacustrine sediments; remnant of low-lying plateau now cut/dissected by dredging followed by erosion, leaving some islands of relatively untouched land; the natural surface is horizontal, and the edges fall away steeply into watercourses, the bank shows very little collapse; surface erosion is very minimal; groundwater level lies at/very near creek-level,(however the preceding metre verges on wet); healthy tea-tree; human influence is probably negligible.

H. ca. 5 cm of tea-tree litter, damp at top, moist otherwise.

1. 0 - 3.8 cm, damp $\frac{4}{4}$ to $\frac{4}{5}$ YR 7.5 browns, decaying organic matter moderate well rooted, virtually no compaction, very porous, soft.

2. 3.8 - 8.3 cm, damp, $\frac{4.5}{4}$ 7.5 YR brown, decayed organic matter with minor silt, well rooted, slight compaction, some matting.

3. 8.3 - 11.3 cm, damp $\frac{3}{1}$ to $\frac{2}{1}$ 10 YR brownish black to black, very humic silty clay, well rooted, poor to fair compaction, crumbly, non-plastic, slight stickiness, some firmness, soft, granular tendency, merges into

4. 11.3 - 43 cm, moist, $\frac{5.5}{3}$ 7.5 YR/10 YR dull yellowish brown clay, massive, compacted, plastic, sticky, soft, not crumbly, rapid decrease in roots merges into

5. 43 - 58 cm, damp to moist, $\frac{5}{2}$ 10 YR greyish yellow brown clay, massive and homogeneous, compact, poor crumbliness, medium plasticity, fairly sticky, soft, rare joints - all with a film of Hg^{o}_{l}, including adjacent outcrops. merges into

6. 58 - 90 cm, moist to west, $\frac{4}{2}$ to $\frac{3.5}{2}$ 10 YR greyish yellow brown, silty clay very similar to above but less sticky, mercury film in joints merges into

7. 90 - 121 cm, moist, $\frac{4.7}{2}$ 2.5 Y dark greyish yellow fine silt, well sorted, horizontal bedding becomes clear, well compacted, very poor plasticity, crumbles into small slabs - faces parallel to bedding, fair development of fine vertical jointing, slimy feel on rubbing, firm, no mottling merges into

8. 121 - 170 cm, moist, $\frac{5}{2}$ 10 YR greyish yellow brown silt as above, slightly more distinct bedding merges into

9. 170 - 220 cm, moist $\frac{4.5}{2}$ 7.5 YR greyish brown, silt, compact, firm, crumbles into blocks (as above), non-fissile, non-sticky,

10. 220 - 770 cm, very moist, 5 YR $\frac{4.5}{3}$ dull reddish brown, stiff plastic, non-sticky (unless reworked thoroughly and wetted), compacted well, non-crumbly - breaks into slabs, fairly well, then behaves plastically, rarely darker at joints, no organic matter or odours, no hydrothermal associations, cold.

TABLE (A.20) WATERS

Zone	No.	Setting	Flow (cm^3/sec)	pH	Gas	Temp. (^oC)	Hg^o_t (ppm)	Cl^- (ppm)	Remarks
1.	1. a.	Pool outlet	~ 5	5:1	W	18-18½			Very quiet activity in mid 1973, no H_2S odour;
		(Small Waitetera)		4*	W	13*	0.0087	19	almost extinct in early 1976.
	b.			3.9-5.0					
	2.	NW part	-	5.2	S	25-30			5 - 70% Sulphur in recent sediments.
		(Waitetera Pond)		2.9-4.4		13.5-16	0.11	210	
	3.	Streamlet	W	-	nil	18-25			Up to 29° 25 cm below surface adjacent Pond
		Damp Course				12-22	~.3	-	HgS present along last 12 m.
	4.	Stream	50	5.6	W	18	.0036		
						12-13		~15	
	5.	Stream	<10		VW	12			
	6.	Stream	70	5.4-4.0		18-19	~.035		
				4.2-3.9*	VW-M	12-13.5	-	15	
	7.	Pool outlet	250	4.5	VW	24-24½	.102	180	20-80% S in Pool and shore sediments near outlet.
		(Waitetera Pond)		2.8*	VW	16	-	-	Water turbid with sulphur.
	8.	Stream	350	5.2	nil	17-18			
				4.8	nil		.0017	49	
	9.	Stream	5000	5.3	~nil	18-18½	.0012		
				5.4		13		14	
	10.	Stream	5000	5.3	W	18	.0012	11	Rare pockets of slow gas percolation through fresh water, limonite on bottom is common.
	11.	Soda Spg	t	6.4	W	29°	.005	22	
	12.	Stream	~100	~6		18			drains an almost flat area.
						12	0.0004	2	
	13.	Damp		5.8	nil	18½	-	-	
	14.	Stream	400	~6	VVW	18	0.0008		part of area has been swamp.
	15.	Spring		5.9	W	25°	-	20	

	16.	Stream	250	~6	nil	18	.0003	-	
	17.	Stream	80	~6.2	nil	17½	.0006	4	partially drains the volcano Ngawha Wamimiti
2.	1.	Stream	100	5.7	nil	17	.0014	12	Fresh water
	2.	Stream	~150	5.4	VVW	17	.0018	13	
	3.	Stream	~350	5.4	nil-VW	17-25	.0017	-	
	4.	Stream	>5000	5.2	VW	17-18	.0013	15	
	5.	Stream	~10000	5.3	nil-M	17-18	.0014	14	One large 'CO_2' gas vent present in stream
	6.	Stream	~10000	5.6	W-S	18-25	.0013	15	Considerable limonite
	7.	Small pool	~nil	~4.5	W	18-22	0.012	-	
	8.	Stream	2250	~4.9	nil	17.5	a. .0045) .0045 b. .0012)	53	Usually faintly cloudy.
	9.		13000	6.7	VW	18.5	.0014	15	Basalt at bottom.
	10.	streamlet	t	-	nil	18-25	.0013	-	
	11.	above waterfall	~15000	6.1 3.9-4.2*	nil	18-25 13	.0014	-	ca. 5 m waterfall over edge of basalt flow
	12.	Bottom	-	6.2 3.5*	nil-VW	18-17	.0013	-	
	13.	a. bog b. seepage	~150	6.6-7.0	nil	18½-20	.0008	-	limonite bog forming from ground water seepage near base of basalt cliff.
	14.	Landslip	~5+t	 2.5-4*	nil-VVW nil-VW	19 13.5	.0017	24 -	Stream is rapidly cutting into chaos breccia, remnant limestone boulders below a series of land flows.
	15.	Stream	~15000	6.0 3.8*	VW VW	19-18	.0013	-	Influx of landslip material, occasionally turns water milky.
	16.	Lake	t	4.1-5.4	VW VW	19 13*	.0155 up to ~0.5 at SW shore	-	Virtually moribund.

17.	Streamlet	12	~6	nil	18	.0013	-	
18.	Stream	~15000	6.6	VVW	19 13.25	.0013	13	
19.	a. Landslip	~100	-	nil	19	.0016	-	large landslips, up to 65 m high.
	b. Stream		6.2	nil	18-75	-		
20.	Streamlet	t	~5	nil	17½	-		
21.	Streamlet	t	~5.1	nil	18			
22.	Stream	400	5.3	nil	18	.0028	-	
			5.4*	nil	12°	-	-	
23.	Stream	~600	-	nil	18.5	.003	-	
24.	Stream	600	~5.0^{+}	nil	18.5	.0037	-	
25.	Pool outlet	t	~6.0	~nil	19	.0016	-	
26.	Stream	1600	5.1-5.8	nil	23-19 16*-5	.014	-	
27.	Stream	1000	4.5-5.9 1.5**	W	24.5-22	.0193	127	
28.	Streamlet	10	5.6-5.0	W-M	17¾-22	.0287-.12	14-27	
29.	Water courses	t	4.5	W-M	20-22	-	-	
30.	a. Pool(s)	t	4.2	M	19	.033	-	5-15% sulphur in sediments
	b. Pool	~0	~4.75	W-M	32-33	.147	44	almost white sulphur precipitate, minor oil, cinnabar
31.	Stream	35	~5	W-M	23-24 16*	.083		
32.	Stream	18	3.9	W	24-24.5	.019 .029	-	
33.	Stream	14	4.0	W-M	26-24.5		-	Very warm bubbling ground on sthn bank. Temperature near 78° C subsurface in mid 1973.
34.	Pool	~t	4.7	M	28-31		27	

35.	Streamlet	2	5.1	W	35-28	ca. 0.65	-	
36.	Stream	1.5	5.4 4.5*	VW	19-24	.0265	-	
37.	Stream	6.5	4.8	W-M	~30 25-30	.46		Ms, HgS, 0.03 ppm Hg filtered
38.	Stream	7.5	5.3	W	24-26	.0315		
39.	Pool O/flow	4.5	5.7	S	43-36°	ca. .70		
40.	Pool 'Tiger'	~1.5	5.8 2* 2.5+	S S S	43.5-57 38-60	.71 1.6	420 795	Cu^{2+}. HgS, Ms adjacent S cemented sediment breccia; 2-15% S.
41.a.	Pool	~nil	~3	W-M	24	.075	16	turbid with S
b.		nil	~3.5	W-M	30	ca. .4	-	oily, turbid with mud and S
42.	v. small pool	nil		M	29	.15		slightly turbid, frothy.
43.	pools	~nil -5	4.5	M	21	present ~.05	-	
44.	Stream	45	3.8	W-M	23-27	.072	-	
45.	Damp Course area	t	4.2-3.7	W	21-23.5	.059	-	
46.	Streamlet	t	-	VW	24-28.5	-	-	
47.	Water from below ground	t ~nil?	- 5.1	W-M	22-25	.35	-	As, Hg^{o}, HgS present
48.	a. damp course b. small pool	t w	~nil 4.1	M	21.5	.046+	-	
49.	Streamlet	3	-	VW	28-29.5	v. high	-	Hg^{o} film
50.	Stream	195	~4.5	W	23-30	v. high ≥.3	39	Hg^{o} films
51.	Damp Water Course	0.5	-	VW	23-24½	v. high	-	Hg^{o} films HgS
52.	Streamlet	6		VW	21-23	.0745	-	HgS, Hg

53.							
a. Damp Courses	t	~3.5	VW-W	23-32	high	-	HgS, Hg^0 General S content of area 10-30%
b. Mainstream		4.3					Sb in adj. main stream seds.
54. Damp Course	w	3.6-4.5	VW-M	21-24	.018	-	10-25% S in silty sediments.
					0.04	-	
55. Freshly dug							
"Groundwater"	~3	5.7	nil	27-22	3.5	-	HgS, Hg^0, 'Sb', DMSO odour, weak gas activity
adj. activity		5.4					broke out after digging.
56. Stream	350	4.7	W-M	27-22	.0435	29	
57. Damp Course	w	-	W-M	18-21	~ .07	-	
58. Stream	~25	5.1	M	24-30°	high locally	-	Some of the stream passes underground.
59. Pool	~350	4.5	W-M	20.5-28°	.0416	29	
60. a. Stream	~100	4.2	W	20.5-22	.019	-	40-80% S in sediments. At base of seds is a great
b. Pool		4.6	M	13°	0.25	18	deal of organic debris.
61. Damp Course	t	-	nil-W	19-20°	.018	-	Alunite, S
62. Stream	125	5.2	nil-VW	19°	low		
63. Stream	50	5.1	VW	18.75-19	.0084	~14	
64. Damp course	t	0	VW	19	~.01	-	S
65. a. Stream	~700	4.8	W	24.5-23	~.09	65	
b.	750	5.2	nil	23-19	~.029	81	
c. c.	750	5.3	VW	19.5	~.0195	84	
66. Damp course	t		W-M	19-27	-	-	
				13-16*			
67. Streamlet	2.5		VW	24-29	.0035	-	
68. a. Streamlet	4	~3.6	VW	22-23	-	-	General Domain area contains 15-60%
b. Main	~1000	4.6-5.2	VW-W	22-24			in sediments
69. Shallow pool	t	~3.7	W	22-23	0.082	-	
70. Streamlet from cold pools	1	~4.1	W-VW	21-22.5	-	-	

	71. Damp course	w	4.2	VW	22	.043		
	72. Pond	~5ml	4.6	W	19-23	.055 (up to ~9ppm at sthn shore)	45	
3	1. a. Lake	-	4.9	W	18-21	0.039 (active part)	-	Thermal activity localised to several square metres on northern shore
	b.	w	ca.5.5	nil	18	.0024	11	
	2. Stream Lower part	~50	-	~nil	18	.003		
	3. Lake	-	4.5	VW-S	17½-21	.0169		
			3-4.5	VW-M	12-17*			
	4. Stream	~20	5.7-4.2	nil-W	18-19	.0031		
	5. Stream	1000	5.2	nil	18½	.013	23	Water is clear and faintly brown
	6. a. Stream	2000	5.7			.0017		Small upstream creek
	b.	100						
	7. Pool	~30	4.9	W	19	.0073	31	Some water nearly clear, most shallow areas are turbid.
			3.5*	W	14-16.5			
	8. Pool	100		W	18-22	.007	-	Mostly clear water, very sulphurous sediments in past. Some alunite.
			2.5-4	W	12-13			
	9. Creek into pool	150		W	18-20	.0049	-	clear water
			4.3		12-13			
	10. Pool	~580	3.6	W-M	18.5-19	.0084	33	pH = 2 @ some pools; mostly turbid, H_2S
	11. Stream	~1250	5.8	nil	18	.0012	-	basalt exposures in course, water is clear
	12. Stream	~100	~6.0	nil	18	-	-	
	13. Stream	~250	~5.9	nil	18	-	-	
	14. Stream	4500	5.6	nil	18	.0025	-	
			3.5*		10.5*			
	15. Stream	~1200	5.3	VW-nil	18	.0023		
	16. Stream	350	5.8	nil	17½	-		

17. Stream W W head	⩾5000	5.9	nil	18	.0016	-		ca 1 km further downstream and at base ca 6 m basalt cliff exposed only in stream.
18. Stream opp.	~400	6.1	nil	18	.0004			Small fresh stream to south and ca. 30 m from above.

BORES	flow	pH	Gas	Temp	[Hg^0]	[Cl^-]	Depth	
1. Ngawha Springs Hotel	nil	6.75	W	53°	.055	ca. 95	~113 m	Contains Fe^{2+} and precipitates limonite on exposure to air.
2. Maori (Domain)	⩽100	6.9	nil	65°	.036	580	~ 20 m	
3. Spa 1	nil	6.5	W	80°			~ 15 m	struck some basalt
4. Spa 2	nil	6.0	W	45°			~ 39 m	
5. Spa 3	nil	5.8	VW	34°			~ 33 m	
6. NI	nil	-	M	19° (surface leak)	present ($\geqslant 3\mu g/l$) in gas	-	~585 m	bottom temp 236° - E & M (1966) (Geothermal water contains more than 0.2 ppm Hg^0 by calculation).

BATHING POOLS (used for bathing, usually emptied daily).

	pH	Temp.	[ΣHg][Hgsol]	
Tranquility (Spa)	6.5	39	0.03	almost clear
Jubilee (Spa)	6.95	49	1.90/0.026	the hottest of all the baths in the basin, very commonly ⩾ 60° at bottom
Waipiro (Spa)	5	37	0.70	
Cinnabar (Spa)	6.5	41	0.14/0.028	
Lobster (Spa)	5	36	1.3	
Velvet (Spa)	4.25	32	2.5/0.26	
Scotsman (Spa)	6.5	40	0.17	
Twin (Spa)	4.5	34½	1.5	S precipitating
Milky Way (D)	6	36	2.3	turbid
Sulphur Way (D)	2.25	17	- 10.029	turbid, S precipitating
Cinderella (D)	6	40	0.050	

Velvet (D)	6	38	0.13/0.092	
Jupiter (D)	6.5	43	0.12	
Universal (D)	6.5	42	0.090	
Venus (D)	6	35	0.15	
Bulldog (D)	6.5	40½	0.038	almost clear

KEY: W = weak (gas flow), S = strong, M = moderate, V = very, t = trickle. pH and temperature measurements were made in both 1973 and 1976; in the former case it was winter and during the latter it was summer, consequently differences arise. Generally both pH and temperature was lower in 1973.

TABLE (A.21) GEOTHERMAL SITES

Zone	No.	Setting	Area (m^2)	Depth (m)	T_{av} (^oC)	Debris	Tar	Gas	H_2O	$Hg_{(o)}$	HgS	S	FeS_2	Remarks
1.	1.	Shore & low terrace	50	-	(cold)	minor	x	minor	S	trace			x	SiO_2 sinter, minor alunite
	2.	Shore	200	>1.5	(cold) - lukewarm		x	minor	S	x	x	(variable ((low mostly)	x	Much rotting kauri debris, adjacent 2nd most active area of pond
	3.	Shore & up to 15 m beyond	100	-	cold	minor	x	var. small	d - s	x	x	(minor (localised (concentration	x	Probably more activity once, never major
	4.	Creek & adj. environment	(20	(- superficial	cold	x	x	w	d - s	x	x	small local cons.	x	
	5.	Flat low-lying Scrub-land	30	-	-	x	x	nil-w	d	x	x	x	x	Patchy activity
	6.	Shore & low terrace	110	variable, ≤5m	18-25	x	x	nil-s	w - s	x			x	(adjacent warmest & most gaseous part of pool
	7.	Barren Scrubland	15	-	cold	x	x	nil	w	x	x	x	x	Locally similar in appearance to altered basalt elsewhere, haematite present
	8.	Low terrace mostly barren	20	>1	cold	var.	x	nil-vw	d - s	x	x	x (trace in low-est parts)	x	
	9.	Pool	60	-	(cold)		x	w	S	x	x	x (in very low parts of thermal horizons)	x	No current deposition of geothermal minerals Water is almost clear, some algae on surface.
	10.	Pool	2600	≥5	19 - 26	mostly covered by S	x	w - s	S	x			x	Turbid, especially the eastern portion
2.	1.	Adj. Creek	40	1 - 10	18 - 60			m	S					Nodules of FeS_2, mostly HgS coated, HgS/Charcoal S ppts in light rain.
	2.	Flat area	300	1 - 15	18 - ?		(often coats large quantities)	w	S		at depth		at depth rare n. surface	$(NH_4)_2SO_4$, H2S, Py.

Zone	No.	Setting	Area	Depth	T_{av}	Debris	Tar	Gas	H_2O	Hg_1^o	HgS	S	FeS_2	Remarks
	3.	Slightly raised flat	100^2	0 - 1	18 - 19	nil	nil	m	~S	x	x		x	
	4.	Slopes in depression	200^2	-	18 - 22	-		w - m	S	x	x		x	
	5.	Pools	5	0 - .25	?	nil	x	m	S	x	x		x	
	6.	Benches & Trench	60	-	-	x	x	w	d		same in trench		same in trench	
	7.	Flats v. active parts	300	2 - 20^+	25 - 90	minor		m - s	S				v. minor	H2S
	8.	Flat some pools	120	2 - 10	24 - 70	var. trees		w - s	↑ S					$(NH_4)_2 SO_4$, Cu^{2+}, S, oil/tar, H2S, (HgS), Ms, (Py), patches on S' cemented sediment breccia.
	9.	Muddy slope collapsing	10	-	~25	minor		w - m	S	minor	x	minor	? nil	
	10.	High bank flat position	12	-	20	x	x	w - m	d	x	x		x	
	11.	Creek bed to close banks	20	>1	21 - 26			w - m	S					FeS_2 pseudomorphs of wood
	12.	Edge of thermal zones by creek	-	-	18 cms	.	x	vw	S	x	x	x	x	Some large logs buried, minor Fe^{3+} near thermal activity
	13.													
	14.													
	15.	Creek - banks	50	-	18 - 19	x	x	w	mostly S	x	x	minor	x	Entrenched, steep entry to thermal area.
	16.	Raised bank	600	3 - 10	~18 - 20	minor	some below surface	nil	d	none above much below surface 10 cm		minor	v. minor	Warm below 10 - 15 cm, crust of S cemented breccia, oily where warm and wet, (HgS).
	17.		150	2 - 5	18 - 20	minor	x	w - nil	~S	minor		some	x	In raised area to NE is much superficial Fe^{3+} efflorescences
	18.													

Zone	No.	Setting	Area	Depth	T_{av}	Debris	Tar/Oil	Gas	H_2O	Hg_l^o	HgS	S	FeS_2	Remarks
1.	19.	Eroding dredging gullies	25	0 - 15	18	x	x	nil - vw	d	rare	x	rare	x	Many areas can form limonite/haematite efflorescences
	20.	Gauged area & flats	150	.5 - 2.5	20 - 23	minor	x	w	S	some	rare, in creek	some	rare, in creek	
	21.	Gauged flats & banks	100	0 - 2	20 - 24	rare	minor	w - m	S	some		minor	some	Hg^o_l commonly coats, organic material, sulphides and some clay lumps.
	22.	Low-lying flat	110	2 - 5	19 - 26		minor	vw	S	minor		v.rare	rare	Much oxidized irons acidic waters mostly Hg^o films on some areas, warm seepages
	23.	Small creek	20	~.5 - 1	? 22	x	x	x	S	some	v.rare	x	x	
	24.	Flat area, fills old pool	350	2 - 6+	20 - 30+	minor	x	vw	S cap cubt			x	x	Orpiment present as a wet broad vein at top of standing water Drops of Hg^o, oil, HgS. Minor H_2S odour + DMSO.
	25.	Lower part bank(s)	10	1.5 - 2	18			nil	low ramp	minor		x	x	HgS with kauri leaves
	26.	Upper part flat below bank	15	1 - 2	18 - 20	minor	x	nil - m	~S	trace	x	trace	x	
	27.	Hollow (raised) sl.	30	.25 - 2	18	x	x	x	damp	trace	x	x	x	altered rock, kaolinized.
	28.	Bank & top (flat) adj. creek	35	.1 - 2	18 - 23	x	x	nil - vw	w - m	film on joint surfaces	rare	x	x	
	29.	Similar	30	.1 - 2	18 - 19	x	x	nil - vw	w	minor	x	x	x	
	30.	Creek & adj. bank & foot slope	60	.2 - 2	~20	x	x to rare	w	S	some films	rare	x	v.rare only in ck.	
	31.	Bank above creek	50	.1 - 1	~18	x	x	x	dry	scattered drops rare films	scattered pcs.	x	scattered + minor dispersion	Only corroded FeS_2; (Hg^o, HgS & FeS_2 usually associated), larger pieces may have dark organic residues included.
	32.	Narrow flat & creek	10	-	~19	x	x	w	S	rare films	minor	x	rare nodules	
	33.	Creek	25	⩾.5	?19 - 20	x rare		w - m	S	minor		x	x	
	34.	Mounds	10	3	~19	rare	x	x	~d	x to trace		minor		Alunite, limonite also present, bedded sediments
	35.	Flat	100	1 - ?	18 - ?	x	x	vw	~S			x	x	Hg^o films on trickles commonly

Zone	No.	Setting	Area	Depth	T_{av}	Debris	Tar	Gas	H_2O	Hg_1^o	HgS	S	FeS_2	Remarks
2.	36.	Streamlet & banks	15	-	19	x	x	vw/nil	~S	minor	minor	x	x	Much haematite crusting on banks
	37.	Mounds	120	3 - 4	18 - 25	some oil at depth	x	vw/nil breaks out at depth	mostly d moist at level of adj. flats	minor	can be high locally	x var. c bed-minor	x rare	Much limonite, some alunite, many buried logs, forest debris, including charcoal. Deeper 2/3rds contains appreciable sulphur, and sulphur rich bands throughout geothermal sediments.
	38.	Streamlet + floor	10	1 - 2	18 - 20	var.	minor	w	S		usually minor	rare	x	
	39.	Raised amphitheatre activity	15	0 - 2	18 - 20	var. mostly rare	x	w	~S	some locally		rare pale films	local pipelet concentrations	
	40.	Steep stream + adj.	20	0 - 3	18 - 21	minor	x	w	~S	local cons.	local cons.	x	rare, only in water course	
	41.	Small series of eroded surfaces	40	0 - 4	18 - 19		x	x - vw	var	~x	x	var.	x	
	42.													
	43.													
	44.	Inside part of meander	25	1 - 2	19 - 26	small pcs	rare	w - m	S	mostly minor gen.	scattered pcs usually on wood + S=	minor	corroded nodules + minor fresh	Some H_2S
	45.	4m steep bank + raised river flat	70	1 - 3	19 - 23	minor	x	x	~S	common on joints	x	x	x	
	46.	Jutting bank	30	1 - 3.5	19 - 24	minor general. but major at bottom	oily water + tar near stream & tree debris	w	S	minor n. surface ubiquitous below 10 cm film on trickles		some	x	Realgar crystals and pulverescent orpiment present in steep bank ca. 3 m above stream
	47.													
	48.	High flat ~dry	50	~2	18 - 19			vw most in creek	~d	traces	traces	often as crusts.	x	S dispersions, crusts and joints. Minor limonite dispersion. Much org. debris.

Zone	No.	Setting	Area	Depth	T_{av}	Debris	Tar	Gas	H_2O	Hg_1^o	HgS	S	FeS_2	Remarks
2.	49.	River bank mostly silty + sand adj. mounds	10	~1 m + .5 - 12	19 - 21	rare	x	x	~S	rare		x	x	
	50.	Gully	25	-	? 18 - 22	x	x	vw	~S	rare films on trickles v.rare droplets locally	x	x minor	x	Haematite, H_2S, rare Hg^o
	51.	Low banks - flat top	15	-	18 - 19	x	x	vw/nil	~d	rare/nil	x	minor/ nil	x	Haematitic crusts at surface + some limonite.
	52.	Mounds	~20	2 - 3	18	x	x	x	d	~nil		x	x	Alunite, rare HgS.
	53.	Amphitheatre + flat adj. ck.	100	1 - 3	18 - 19	var. mostly minor	x	w	~S	~nil	x	var. locally high	x	Alunite on most wood.
	54.	Flat	10	-	18	nil/rare near surface	x	x	S	x	x	x	x	
	55.	Flat stream pool	6	-	19	x	x	w	S	~nil	x	some	x	
	56.	Stream mostly sub	~50	⩽.5	19 - 22		x		var. w - s	~nil	x	var.	x	S crusted leaves common
	57.	Pool + environs	250	2 - 5 m	~20 - 24	var. mostly low at surface high at depth	x	w - m	S	~nil	x		x	Sediments ⩾90% S.
	58.													
	59.													
	60.	Flat	300	2~4 m	18 - 22 ~	higher depth where major constituent	x	w - m	w - s	~nil	x		x	
	61.	Flat	200	2 - 5 m	+		x	w	w	~nil	x		x	
	62.	Pool clear	7	~3.5	?		x	m	s	nil	x		x	Many logs, precipitating pale S.

Zone	No.	Setting	Area	Depth	T_{av}	Debris	Tar	Gas	H_2O	Hg_1^o	HgS	S	FeS_2	Remarks
2.	63	Gentle slope	5	-	~18		x	vw	~w	~nil	x		x	Many fallen trees, all tops pointing down into centre of hollow.
	64	Flat	12	~.5 - 1	18 - 19	sl. more debris below surface	rare	~nil	w	nil	x	minor	x	Some MnO_2 in ground joints at extreme NW.
	65	Isolated extent flat	10	-	18	minor at surface much below	x	x	w	x	x	some in joints other debris below esp leaves	x	MnO_2 in joints
	66	Stream flat btm ~3m banks	15	>1	18 - 19	most in adj. bank-strataed ~none in creek	rare	w	S	x	x	rare	x	Soil at top of bank - profile J
	67	Stream as above	20	>1	18	confined to banks most is peaty	x	w/vw	~S except upper banks	x	x	in banks most.	x	Soil, much S in present in lower 2/3rd of veg. debris in banks. Where S is not present (mostly upstream) tar has formed.
	68	Entrenched stream	10	.5	18½	minor	nil	vw	~S	x	x	x	x	
	69	Old site of surface activity	5	super-ficial	18			w	d	x	x		x	
	70	~as 69	20	"	18			x	"	x	x		x	
	71	~as 70	4	"	18			x	"	x	x		x	
	72	~as 71	10	1.5	18	var.		x	w - d	x trace	x		x	
	73	~as 72	6	super-ficial	18	minor	minor	x	d	x	x		x	
	74.	~as 73	15	1 - "	18			faint H_2S small	d	x	x		x	
	75	~as 74	5	" - 1	18	minor	x	x	d - w	x	x	x	x	
	76	Main stream	-	-	? 19 - 22	x	x	x	S	x	x	x	x	Soil is present almost into creek, no thermal activity past or present
	77	Upstream at domain flat + SW edge of clear area	25	1 - 1.5	~19	x	x	w	S	x		x	x	Minor limonite precipitates from stream
	78	Higher part of river flats	450	0 - 1	18 - 21	x	x	nil/vw	~S	x traces	traces	traces	x	Minor Fe^{3+} on some surface
	79	Adj. streamlet/ soak	30	0 - 75	18 - 20	x	x	w	w	traces	x	x	x	

Zone	No.	Setting	Area	Depth	T_{av}	Debris	Tar	Gas	H_2O	Hg_1^o	HgS	S	FeS_2	Remarks
2.	80.	W & SW Perimeter	50	0 - .5	18	x	x	vw/nil	~d	x	x	x	x	
	81.	S Perimeter	250	small	18 - 20	x	x	vw locally	~d	tr.	x	some in joints	x	
	82.	Perimeter bordg stm let course	200	-	18	x	x	vw locally	d - s	x	x	rare	x	
	83.	Shallow dep of	500	1 - 3	19 - 24	x	x	w	S			minor	x	
	84	Mound + adj. flat	100	1.5 - 5	-	x	x	vw - w	d - s	x	trace	in lower levels	x	Altered clay many fossil gas holes
	85	Low lumps	200	1 - 4	18	x	x	x	d	x		x	x	
	86	Cold pools	400	.5 - 4	18 - 22	x	x	w - m	S	x	x		x	
	87	N Flat adj. along river	1000	1 - 5	19 - 22	x	x	w - m	S	minor	some var.		x	S precipitating in all pools, probably no current HgS, HgS is buried in silts.
	88	Flat	700	2 - 4	19 - 20	x	x	vw	S	minor	x		x	
	89.													
	90.													
	91.	Bank terrace old	15	≤1m	18	x rare	x	vw	~d	traces	x	esp in joints	x	
	92	Offside of Spa Hotel cutting	20	embank-ment of 1.5 m	18	x	x	vw	~w		x	x	x	
	93	SW low terrace + shore	40	1 - 3+	18 - 20 (drilling shows org material at 0-15 m)	x	x	vw - w	w - s	traces	rare traces	x	x	
	94	S + SW part of pool + proximal shore		1 - 4	18 - 24	x	x	w	S	traces	traces	x	x minor at warm spots	
	95	SE (at onetime in flow)	150	1 - 4.5	18 - 22	x	x	nil - w	S		rare	x	minor at warm spots	
	96	E	400	1 - 3	18 - 21	x	x	vw/nil	S	x	x	x	x	

Zone	No.	Setting	Area	Depth	T_{av}	Debris	Tar	Gas	H_2O	Hg_1^o	HgS	S	FeS_2	Remarks
2.	97.	NW region	2000	-	18	? x	-	vw mostly nil	S	x	x	x	x	Least active part
	98	Outflow environs	200	-	+8	x	x	x	S	x	x	x	x	Virtually inactive now, being over grown rapidly by ti-tree and gorse.
	99.	Large area of terrace	5000	.	18	x	x	d	d	x	x	x	x	
	Baths													
	Waiapawa Lake		50000 150	-	~18	x	x	nil - w	S	x	x	traces	x	Most activity now confined to $150m^2$ at SW end of lake, where there is much sand cold sulphurous gases.
3.	1.	Lake	20000	-	18	minor locally high	x	nil vw locally along extreme N end.	S	x	x	x	x	Lake proper is inactive
	2.	Low lying shore	150	-	18		x	w	S	x	x	minor	x	Low ebb of activity
	3.	Creek + adj. environs	25	-	18	x	x	vw - nil	w - s	x	x	x only at lake	x	
	4.	Shore	350	.5 - ⩾2	18 - 22		x	w - vw	S	x	x	some	x	~45000 m^2 (includes lake)
	5.	Lake	1500	<25	18 - 20		x	w - s	S	x	x	minor	x	Several large vents in SW give off majority of gas
	6	Scrub land close to lake	500	-	18	x	x	-	~d	x	x	x	x virtually	alteration ⇒ basaltic; extinct, A few pieces of basalt nearby.
	7	Lake	10000	-	18		x	nil - vw	S	x	x	~ x	x	Virtually inactive except along southern shore, rare along northern shore.
	8 ~steep	Shore	200	-	18 - 19	minor	x	vvw - nil	d - s	x	x	x	x	Almost extinct.
	9	Shore	150	-	18	minor	x	nil	d - s	x	x	x	x	Extinct

Zone	No.	Setting	Area	Depth	T_{av}	Debris	Tar	Gas	H_2O	Hg_l^o	HgS	S	FeS_2	Remarks
3.	10.	Shore + creek environs	200	0 - >3m	18 - 20		x	w - nil	S	x	x	var. local concs.	x	Slight activity over wide area, recent mud buries much plant debris has S dispersed in ~lower 2/3rds. Goethite found in creek towards lake
	11.	Lake	20	-	18	-	-	w - m	S	x	x		x	Small area of gas activity
	12.	Shore	1000	-	18		x	nil - vw	S	x	x	x	x	Almost extinct
	13.	Creek	-	-	18	minor	x	x	w - s	x	x	x	x	No activity
	14.	Shore	50	1 - 2	18	~peat	x	vw	S	x	x	x	x	Extinct probably active once
	15.	Large terrace	~60000	0 - 3.5	18 - 19	peat mostly	x	x	S	x	x	x	x	Now a swamp - 2 drainage levels only a few cm apart. Minor S found in lowest part adj. present lake - none more than 50 m away.
	16	Lake & Shore (U.S.P.)	1350	0 - 3.5			x	w - m	S	x	x		x	most acitivty is confined to SW
	17	" (M.S.P.)	2500	0 - 3			x	w	S	x	x		x scattered in site	Most activity at W end & centre. Solid S below peat to NW
	18	" (L.S.P.)	3750	0 - 3	18 - 23		x	w - m	S	x	x		x	Most activity confined to W, turbid S in E water more translucent

KEY: x = none present, d = damp, S = saturated, s = strong flow, pcs = pieces, cons = concentrations = concs, Ms = marcasite, Py = pyrite, org = organic, n. = near. U.S.P. = Upper Sulphur Pond, M.S.P. = Middle Sulphur Pond, L.S.P. = Lower Sulphur Pond, in the remarks column S refers to elemental sulphur, S, E, W and N are also used to refer to south, east, west and north.